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THE INSTITUTE OF PETROLEUM

AN Ordinary General Meeting of the Institute of Petroleum was held at 26 Portland Place, London, W.1, on 9 March 1955, the Chair being taken by G. H. Thornley, M.Sc., a vice-president of the Institute.

The General Secretary read the minutes of the previous meeting, which were confirmed and signed as a correct record. He also announced the names of members elected since the previous meeting.

The Chairman, introducing the author of the paper to be presented, said: The title of tonight's paper is "The Viscosity of Liquid Hydrocarbons." It is being presented by Mr L. Grunberg, who is a fellow of this Institute, and a graduate of the Oil Department of Birmingham University, where he studied under the late Professor Nash. Working with Dr (now Professor) Nissan, his research interests were soon directed towards the viscosity of liquids, and in particular, of hydrocarbons. Although he left the department in 1942 to take up an appointment in an industrial research organization, his interests in the more academic aspects of research continued, and in collaboration with Nissan, he published a number of papers on viscosity. In 1951, he joined the Department of Scientific and Industrial Research, as deputy to the head of the Lubrication Division in the newly established mechanical engineering research organization. This brought to him a number of highly absorbing and new research projects, such as the study of defect structures in freshly deformed surfaces, by means of Geiger counters.

The paper to be presented tonight, and some recently published work on the viscosity of solutions, testifies however, that he has not abandoned his interest in the study of hydrocarbons and in viscosity in particular, which was instilled into him in the oil department of Birmingham University some fifteen years ago.

The following paper was then presented in summary by the author:

THE VISCOSITY OF LIQUID HYDROCARBONS *

By L. GRUNBERG † (Fellow)

SUMMARY

The simple exponential equation $\eta \propto e^{\Delta E/RT}$ relating viscosity and temperature cannot be applied to hydrocarbon oils, since changes in temperature produce changes in the state of order and in the configuration of molecules. These changes are studied by separating the free energy term into an energy factor and a configurational entropy. For studying changes in configurational entropy the atmospheric boiling point is chosen as the reference state, since it corresponds to the highest degree of disorder possible in the liquid at atmospheric pressure. It is found that for rigid hydrocarbon molecules the configurational entropy is positive, whilst it is negative for more flexible molecules. Similar results are obtained if the reference temperature is chosen arbitrarily, without considering the equation of state of the liquid. An equation embodying three constants and requiring measurements at three temperatures is proposed to characterize the viscosity–temperature relationship of hydrocarbon oils.

INTRODUCTION

PETROLEUM technologists are greatly interested in the variation of the viscosity of liquid hydrocarbons with the temperature. One of the simplest problems encountered is the extrapolation of data to temperatures at which no experimental values are available. The ASTM charts based essentially on Walther's equation [1] are useful for this purpose, although the fundamental basis of that equation has yet to be found. More often, however, viscosity is used as a means of classifying hydrocarbon oils, and it is assumed that the viscosity–temperature relationship, expressed for instance as the viscosity index, does this in an unambiguous manner. Since fundamental knowledge in this field is sorely lacking, it seems appropriate to gather a few facts on this subject.

A most striking discrepancy exists between the equation for the dependence of viscosity on temperature proposed by physical chemists and those which petroleum technologists find useful. The former, deduced on the basis of simple models, and hence applicable to simple liquids, usually suggest that

$$\eta \propto e^{\Delta E/RT} \quad . \quad . \quad . \quad . \quad (1)$$

where η = the dynamic viscosity; ΔE = a free energy; R = the gas constant; T = the absolute temperature. Equation (1) has so far not been very useful for describing the viscosity–temperature relationship of hydrocarbon oils, and one cannot escape the conclusion that such oils are more complex than the models for which the equation has been derived. The present paper attempts to show how complexity of molecular structure and other factors can lead to deviations from equation (1) for liquid hydrocarbons.

REVIEW OF THEORIES FOR THE VISCOSITY OF LIQUIDS

Although equation (1) was proposed by de Guzman [2] as early as 1913, it was not until 1934, after the publication of its independent discovery by Andrade,[3]

* MS received 23 December 1954.

† Lubrication and Wear Division, Mechanical Engineering Research Laboratory, Department of Scientific and Industrial Research, Thorntonhall, Glasgow.

that it became generally accepted. This was followed shortly by the theories of Frenkel [4] and Eyring,[5] which introduced the exponential term into more detailed equations. Although Frenkel's theory was based on the model of a highly ordered, quasi-crystalline liquid, and that of Eyring on the assumption of complete disorder, they both lead to similar expressions, in which the variation of the viscosity with the temperature was expressed as an exponential term similar to (1). The next stage in the development of the theory of viscosity was the publication by Born and Green [6] of a general theory of molecular fluids. Apart from the potential energy function the radial distribution of molecules was considered of importance. This theory has so far been applied only to mono-atomic liquids.

The theories mentioned consider molecules to be hard and perfectly elastic spheres, and when dealing with highly complicated and possibly flexible molecules, such as hydrocarbons, the details of the theories can be applied only to a limited extent. This was first realized by Bondi,[7,8] who attempted to develop Eyring's theories and considered flexible and rigid hydrocarbons. Grunberg [9] considered the same problem independently, and based his conclusions on equation (1).

When studying the viscosity of hydrocarbons it is necessary to consider, in addition to the possible flexibility or rigidity of the molecules, also the state of order or disorder existing in the liquid. Several attempts have been made to use viscosity as a measure of the state of molecular order existing in liquids. Mack [10] suggested that the fluidity, *i.e.* the reciprocal of the viscosity, should be proportional to the degree of disorder and Dienes [11] proposed an equation

$$\eta = \frac{\eta_0}{2} e^{\Delta E/RT}[e^{U/R(T-T_0)} + 1]$$

where U = the energy of ordering and T_0 = a characteristic temperature. Moore, Gibbs, and Eyring [12] applied themselves more specifically to the problem of order–disorder in hydrocarbon liquids. From a study of the variation of ΔE and other physical data with the temperature they concluded that three liquid regions may exist in liquid hydrocarbons: a quasi-crystalline region, a region in which "libration" was possible, and a region in which free rotation on the long axis of the molecules occurred.

THE STRUCTURE OF HYDROCARBON LIQUIDS

It is well-known that long-chain paraffin molecules form fully stretched zig-zag chains in solid crystals and are completely "crumpled" or coiled upon themselves in the vapour. The former can easily be deduced from X-ray diffraction measurements and the latter from the low values of the collision diameters calculated from gaseous viscosity. The change from the fully stretched to the "crumpled" configuration can be expected to occur at some point in the liquid range, and the degree to which this transition has taken place will be of great significance in viscous flow.

Before pursuing this in detail it is necessary to reiterate first the behaviour of molecules in simpler types of liquids, in which the added complication of molecular flexibility does not exist.[13] The arrangement of the molecules in a liquid does not differ materially from that of the corresponding solid except in the following respects: (1) the order or symmetry exists over distances equal to a few molecular diameters but is lost over long distances; (2) the order changes in time as well as in space; (3) a large number of unoccupied sites exist; (4) the rotational degrees of freedom are less impaired. For hydrocarbon liquids it is necessary to consider also the extent to which the structure of the molecules affects the rotational degrees

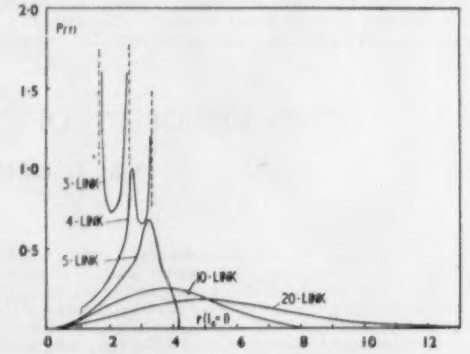

FIG 1

GEOMETRICAL PROBABILITY OF DISTANCE BETWEEN ENDS OF HYDROCARBON CHAINS AS A FUNCTION OF THE NUMBER OF C–C BONDS (LINKS) [15]

of freedom. This involves the question of hindered internal rotation in hydrocarbons, which has recently been reviewed by Aston.[14] In ethane, for instance, the two methyl groups may in extremes take up one of two positions, so that the C–H bonds lie either above each other or are displaced by an angle of 60°. The potential barrier favouring the latter position is 2·75 kcal mol^{-1}, *i.e.* considerably greater than the thermal energy of the molecules at temperatures in the liquid range of ethane, and it can be expected that in liquid ethane the C–H bonds will be displaced relatively to each other. The same considerations when applied to propane suggest that two stereoisomers, namely the *cis* and *trans* forms, can exist and that the potential barrier favouring the latter is about 3·3 kcal mol^{-1}. For *n*-butane the *trans* form is favoured by a potential barrier of about 3 kcal mol^{-1}. From these data one can conclude that an extended shape of hydrocarbon chains is favoured, owing to the repulsion of the end-methyl groups. For hydrocarbons higher than C_4 the greater separation of the end-methyl groups and free rotation round intermediate C–C bonds probably reduces the hinder-

ing potential and leads to a lesser degree of extension of the chains. Similar conclusions can be reached from purely geometrical considerations. Treloar [15] obtained the geometrical probability of the distance between the ends of a hydrocarbon chain as a function of the number of links in the chain, *i.e.* C–C bonds, as shown in Fig 1. For the three-link chain (*n*-butane) the probability tends to infinity at two definite distances. The smaller distance corresponds to the *cis* position, unlikely to occur at low temperatures, and the greater distance to the *trans* position. The four-link chain (*n*-pentane) has an intermediate maximum, but the probability still tends to infinity, when the chain is fully extended. With increasing chain length freedom of rotation and crumpling of the chain increases, both on purely geometrical and on thermodynamic grounds. If a hydrocarbon chain is branched or attached to a naphthenic or aromatic ring system additional hindering potentials arise and a " stiffening " of the molecules ensues.

The picture of molecules in a hydrocarbon liquid appears to be exceedingly complicated and the effect of substituted groups and of temperature on the effective shape of molecules difficult to assess.

THE VISCOSITY–TEMPERATURE FUNCTION

In order to formulate the viscosity–temperature function in a manner which would take into account the changes which temperature brings about in a hydrocarbon liquid, it is necessary to consider the changes in structural entropy of the liquid, the entropy changes associated with molecular configuration, those associated with *inter*- and *intra*-molecular interactions, and so forth. Such a treatment, even if it were possible at the present state of our knowledge, would lead to a different equation for every type of compound, and would obviously be impractical. The best alternative is to use the simplest possible type of equation and try to deduce from the various degrees to which various compounds conform or deviate from the equation the influence of molecular structure. Eyring,[5] Bondi,[7, 8] and others used an equation of the type

$$\eta_l = \eta_0 e^{\frac{\Delta H - T\Delta S}{RT}} \quad . \quad . \quad . \quad (2)$$

in which the free energy ΔE is split into an energy ΔH, analogous to the heat of reaction in chemical processes and an entropy term $T\Delta S$. Although formally justified, it seems preferable to base changes in entropy on some reference state and define explicitly whether the thermodynamic quantities refer to constant pressure or constant volume. Most data for viscosity were obtained at atmospheric pressure, and it is therefore useful to define the thermodynamic quantities as referring to constant pressure, *i.e.* 1 atm. The reference temperature could be chosen quite arbitrarily, say at 25° or 100° C, but it seems preferable to relate it to some point on the equation of state of the liquid. Two points suggest themselves readily, namely the melting and boiling points at atmospheric pressure. At the melting point the degree of order in the liquid would be at a maximum, whilst at the boiling point it would be at a minimum. Several investigators [16, 17] have found that viscosity can be correlated at the boiling point, and if it is further considered that it may be desirable to choose a state in which the rotational degrees of freedom are developed to a large extent, the choice of the boiling point at atmospheric pressure seems preferable. Equation (2) in logarithmic form reads :

$$\log_{10} \eta_p = \log_{10} \eta_{0_p} + \frac{\Delta H_p}{2{\cdot}3RT} - \frac{\Delta S_p}{2{\cdot}3R} \quad (3)$$

when the subscript p denotes the fact that the quantities are considered at atmospheric pressure. If one subtracts from equation (3) the corresponding equation at the absolute boiling temperature T_B

$$\log_{10} \left(\frac{\eta}{\eta_B}\right)_p = \frac{\Delta H_p}{2{\cdot}3R}\left(\frac{1}{T} - \frac{1}{T_B}\right) - \frac{(\Delta S - \Delta S_B)_p}{2{\cdot}3R} \quad (4)$$

By definition

$$(\Delta S - \Delta S_B)_p = \int_{T_B}^{T} c_p d \ln T \quad . \quad . \quad (5)$$

where c_p is a specific heat factor analogous to the heat capacity at constant pressure. Writing

$$\frac{T}{T_B} = \tau$$

and introducing (5) into (4) one obtains

$$\log_{10} \left(\frac{\eta}{\eta_B}\right)_p = \frac{\Delta H_p}{2{\cdot}3RT_B}\left(\frac{1}{\tau} - 1\right) - \frac{c_p}{R}\log_{10}\tau \quad (6)$$

Equation (6) indicates that the ratio of the viscosity at any temperature to that at the boiling point is a unique function of the absolute temperature divided by the absolute boiling temperature provided the ratio $\Delta H_p/T_B$ and the specific heat factor c_p are the same.

In several instances a correlation of η_l with τ has been found useful. Nissan [18] found that the viscosity of all the *n*-paraffin above C_6 could approximately be represented by a series equation in terms of τ

$$\log_{10} \eta_{\text{paraffin}} = 4{\cdot}283 - 18{\cdot}572\tau + 17{\cdot}505\tau^2 - 5{\cdot}900\tau^3 \quad (7)$$

and it has also been suggested [9] that the correlation of the viscosity of other hydrocarbons is possible by dividing the viscosity by the viscosity of a *n*-paraffin (equation (7)) at the same value of τ.

A special feature of equation (6) needs to be noted. If the difference

$$\log_{10} \frac{\eta_l}{\eta_{lB}} - \frac{\Delta H}{2{\cdot}3RT_B}\left(\frac{1}{\tau} - 1\right)$$

is positive, then the difference in entropy, $\Delta\sigma$ is positive, whilst the specific heat factor c_p is negative, since generally $\tau < 1$ and $\log_{10}\tau < 0$. If the difference $\Delta\sigma$ is negative c_p is positive. In the present paper it has been found useful to express the results in

terms of $-\Delta\sigma$, so that to consider results positive, when the specific heat factor c_p was positive.

An equation similar to (6) can be set up also when using a reference temperature other than the boiling point. This is, of course, necessary for higher hydrocarbons, for which the atmospheric boiling point may either not be available or cannot be attained, since it lies in a temperature range in which thermal cracking occurs. Let T^* be the absolute reference temperature chosen; η^*, the viscosity at T^*; τ^*, the ratio T/T^* and ΔH^* and c^* the corresponding thermodynamic constants, then

$$\log_{10}\left(\frac{\eta}{\eta^*}\right)_p = \frac{\Delta H_p^*}{2{\cdot}3RT^*}\left(\frac{1}{\tau^*}-1\right) - \frac{c^*_p}{R}\log\tau^* \quad (8)$$

The relationship between ΔH^*_p and ΔH_p can now be established by suitable transformations which yield

$$\frac{\Delta H^*_p}{2{\cdot}3RT^*}\left(\frac{1}{\tau^*}-1\right) = \frac{\Delta H_p}{2{\cdot}3RT^*}\left(\frac{1}{\tau^*}-1\right) - \frac{(c_p+c^*_p)}{R}\log_{10}\tau \quad (9)$$

and hence that ΔH^*_p can be greater or smaller than ΔH_p according to whether $(c_p + c_p^*)$ is negative or positive.

The description of all the changes which may occur in a liquid into a single specific heat factor enables only an overall assessment to be made of the various processes involved, but when studying groups or classes of compounds over wide ranges of temperature the importance of one or the other processes can be suggested.

INVESTIGATION OF EXPERIMENTAL MATERIAL

For a systematic investigation of the equations proposed it was necessary to assemble data for the viscosity of hydrocarbons in suitable form. The collection of data was published in a paper.[19] Since then the American Petroleum Institute[20] has published reliable data for a few hydrocarbons. The calculations of the various constants is, however, laborious, and in the present paper the results of a few groups of hydrocarbons can be presented.

RESULTS BASED ON BOILING POINT AS REFERENCE TEMPERATURE

n-*Paraffins*

As mentioned earlier, the viscosity of this series of compounds was investigated by Nissan,[17,18] who, on the basis of the data available at the time, derived the series equation (7) for the *n*-paraffin above C_8. It appeared of interest to investigate to what extent the more recent data obtained under the API project conformed to equation (7). The API data extend over the wide temperature interval of $-190°$ to $+340°$ C. Nissan's correlation predicted that at the boiling point ($\tau = 1$) all *n*-paraffins should have the same viscosity, namely 0·207 cp. Table I shows the values of η_B obtained from a careful interpolation and extrapolation of the API data.

TABLE I

Values of η_B *for* n-*Paraffins*

n-Paraffin	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}
η_B, cp	0·204	0·206	0·210	0·209	0·209	0·208	0·207	0·206
n-Paraffin	C_{13}	C_{14}	C_{15}	C_{16}	C_{17}	C_{18}	C_{19}	C_{20}
η_B, cp	0·205	0·204	0·202	0·201	0·200	0·20	0·20	0·20

Considering that even the API-data report the viscosity near the boiling point for the *n*-paraffins above C_{18} only to two significant figures, this prediction of Nissan's correlation appears exceedingly

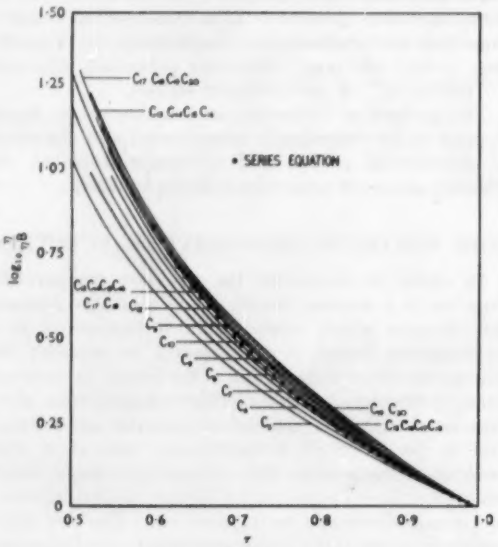

FIG 2

COMPARISON OF API DATA[20] WITH SERIES EQUATION[18]

good. Less satisfactory is, however, the prediction for the variation with temperature, particularly for the lower *n*-paraffins at low values of τ and for the higher *n*-paraffins at high values of τ (Fig 2). This discrepancy can be easily understood, since the series equation was derived essentially on the basis of data for small τ's of the higher hydrocarbons and for large τ's of the lower hydrocarbons.

The correlation shown in Fig 2, however, makes it clear that the constants in equation (6) cannot be expected to be the same for all the *n*-paraffin, but will show a systematic variation with increasing length of the hydrocarbon chain. In order to obtain the constants, $\log_{10}\eta/\eta_B$ was first plotted against $\left(\frac{1}{\tau}-1\right)$ and the initial tangent equal to $\Delta H_p/2{\cdot}3RT_B$ passing through the origin was determined. Table II gives the values of $\frac{\Delta H_p}{2{\cdot}3RT_B}$ for the *n*-paraffins C_5 to C_{20}.

TABLE II

$\frac{\Delta H_p}{2{\cdot}3RT_B}$ *for* n-*Paraffins*

n-Paraffin	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}
$\frac{\Delta H_p}{2{\cdot}3RT_B}$	1·223	1·273	1·357	1·385	1·430	1·470	1·500	1·520
n-Paraffin	C_{13}	C_{14}	C_{15}	C_{16}	C_{17}	C_{18}	C_{19}	C_{20}
$\frac{\Delta H_p}{2{\cdot}3RT_B}$	1·550	1·568	1·583	1·600	1·614	1·630	1·641	1·655

The function $\frac{\Delta H_p}{2{\cdot}3RT_B}\left(\frac{1}{\tau}-1\right)$ and the difference

$$\frac{\Delta H_p}{2{\cdot}3RT_B}\left(\frac{1}{\tau}-1\right)-\log_{10}\frac{\eta_l}{\eta_B}=-\Delta\sigma$$

were calculated.

The results show a gradual increase of $\Delta H_p/2{\cdot}3RT_B$ with increasing length of the paraffin chain, but the variation of the entropy term $\Delta\sigma=\frac{c_p}{R}\log_{10}\tau$ is, however, more complicated. Fig 3 shows $-\Delta\sigma$ versus $-\log_{10}\tau$ for the *n*-paraffins C_5 to C_9. Several

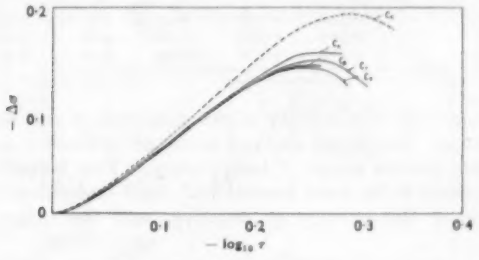

FIG 3

ENTROPY CURVE FOR *N*-PARAFFINS C_5–C_9

interesting features of the curves can be noted. All the *n*-paraffins with an odd number of carbon atoms show the well-known melting point anomaly, *i.e.* the liquid range is extended to lower temperatures (higher values of $-\log_{10}\tau$), but this particular range is characterized by a negative slope, which is absent in *n*-paraffins with an even number of carbon atoms. This behaviour can best be explained by the repulsion of the end-methyl groups, which in odd numbered paraffins would tend to approach each other more closely than in even numbered ones. The curves become flatter and gradually approach straight lines. As the boiling point is approached ($-\log_{10}\tau\longrightarrow 0$) the curvature is reversed. This behaviour suggests that there is a gradual change of the configuration of the hydrocarbon chains from the parallel arrangements immediately above the melting point to "crumpled" or coiled up molecular configurations near the boiling point. Fig 4 shows the results of the calculations for the *n*-paraffins C_{10}–C_{14} on which the curves for C_5 and C_9 are also given in order to show the relationship with the curves on Fig 3. It is interesting to note the shift in the position of the configurational entropy curves with increasing chain length. From C_5 to C_9 this entropy decreases with increasing chain length. For C_5 owing to the close proximity of the end-methyl groups coiling up of the molecule is impeded, but this becomes more probable with C_6, which can curl up

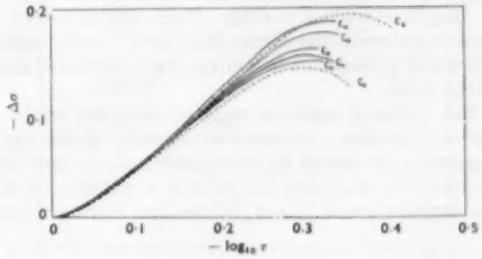

FIG 4

ENTROPY CURVE FOR *N*-PARAFFINS C_{10}–C_{14}

into itself to approach the hexagonal symmetry of benzene or *cyclo*hexane. As the chain lengthens further, the entropy decreases until another half of the six-membered chain has been added in C_9. Still further lengthening of the chain is accompanied by an increase in the configurational entropy. This can be seen from the entropy curves for C_{10} and C_{14} and from those up to C_{20} in Fig 5. Increase in chain length also decreases the region of negative slope, which almost completely disappears for C_{19}.

The change in molecular configuration with temperature is still better followed by considering the change in the specific heat factor c_p. The definition of this factor according to equation (5) is only fully valid over a relatively narrow temperature range, and c_p is hence best expressed by $Rd\Delta\sigma/d\log_{10}\tau$. This was determined for C_5 and C_{20}, and the results are shown in Fig 6. The curve for C_5 shows that between $\tau=0{\cdot}47$ and $\tau=0{\cdot}62$ c_p increases continuously. At

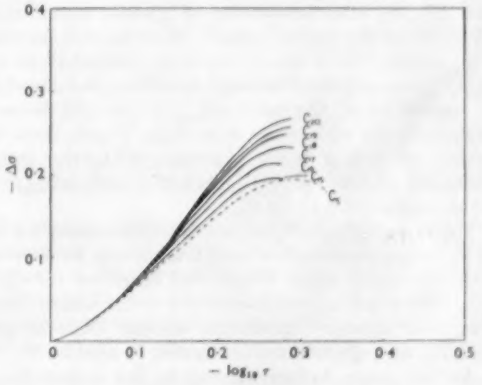

FIG 5

ENTROPY CURVE FOR *N*-PARAFFINS C_{15}–C_{20}

the latter temperature the curve changes direction gradually and reaches zero at the boiling point. It appears likely that up to $\tau=0{\cdot}62$ the C_5-chain is fully extended, and that within this range the flow

process involves elongated, relatively rigid molecules. Above $\tau = 0{\cdot}62$ gradual crumpling of the chain sets in, and the coiling-up process approaches completion near the boiling point. The C_{20} chain behaves similarly, except that the turning point of the c_p-curve is displaced to $\tau = 0{\cdot}70$. This displacement is probably due to the larger number of configuration, which can correspond to a more or less extended shape of the chain.

The above hypothesis suggests that the relatively low temperature coefficient of viscosity of the higher *n*-paraffins is caused by configurational changes from extended to crumpled chains, and is at variance with the explanation of Moore, Gibbs, and Eyring,[12] based

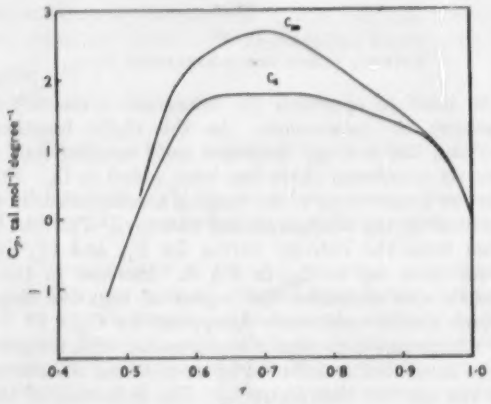

FIG 6

SPECIFIC HEAT FACTORS FOR *N*-PENTANE AND *N*-EICOSANE

on gain of freedom of rotation about the long axis of the chain and that of Bondi [7] based on a process of co-operative flow. The hypothesis suggested here can be checked by a comparison of the entropy of flow $\Delta H_p/T_B$ with the entropy of internal vaporization $\Delta E_{vap}/T_B$ at the boiling point. If at this temperature a *n*-paraffin chain would be fully extended in the liquid phase and would change to a crumpled structure on vaporization, the ratio $\Delta E_{vap}/\Delta H$ would decrease monotonically with increase in chain length, since the degree of coiling would increase with the latter. Table III shows $\Delta E_{vap}/T_B$, $\Delta H_p/T_B$, and $\Delta E_{vap}/\Delta H_p$ for the *n*-paraffins C_5 to C_{20}.

The ratio $\Delta E_{vap}/\Delta H_p$ is practically constant for the whole series, although a slight tendency to decrease with increasing chain length can be noted for C_5 to C_{11}. The ratio approximates the value which Grunberg and Nissan [13] predicted on the basis of geometrical arrangements of molecules in liquids.

At this stage, before turning to the *iso*paraffin, it appears appropriate to discuss the lower members of the *n*-paraffin series, which have much in common with the former, such as the close proximity of methyl groups. The relevant constants for the *n*-paraffins C_1 to C_3 are given in Table IV. Fig 7 shows the curves of $-\Delta\sigma$ *v*. $-\log_{10}\tau$. Methane shows a very slight positive entropy, and one can assume that this is

TABLE III

n-Paraffin	$\frac{\Delta E_{vap.}}{T_B}$, E.U.	$\frac{\Delta H_p}{T_B}$, E.U.	$\frac{\Delta E_{vap.}}{\Delta H_p}$
C_5	19·05	5·638	3·378
C_6	19·37	5·820	3·327
C_7	19·79	6·110	3·238
C_8	20·05	6·328	3·168
C_9	20·42	6·535	3·123
C_{10}	20·63	6·715	3·118
C_{11}	20·99	6·850	3·063
C_{12}	21·26	6·948	3·060
C_{13}	21·53	7·085	3·040
C_{14}	21·78	7·167	3·038
C_{15}	22·05	7·235	3·047
C_{16}	22·33	7·312	3·053
C_{17}	22·65	7·380	3·070
C_{18}	22·86	7·450	3·068
C_{19}	23·04	7·495	3·074
C_{20}	23·18	7·565	3·065

TABLE IV

n-Paraffin	η_B, cp	$\frac{\Delta H_p}{2{\cdot}3RT_B}$,	$\frac{\Delta E_{vap.}}{T_B}$, E.U.	$\frac{\Delta H_p}{T_B}$, E.U.	$\frac{\Delta E_{vap.}}{\Delta H_p}$
C_1	0·118	0·960	16·33	4·39	3·72
C_2	0·168	1·010	17·84	4·62	3·86
C_3	0·210	1·104	18·34	5·04	3·64

connected with rigidity of the molecules of this compound. The liquid state of methane extends over a very narrow range of temperature. This behaviour appears to be quite general with rigid molecules. In ethane the entropy is negative, and the range of

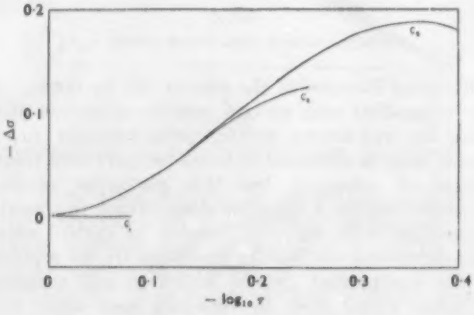

FIG 7

ENTROPY CURVES FOR *N*-PARAFFINS C_1–C_3

temperature over which this compound exists as a liquid is greater than in methane. These factors are still more marked in the case of propane.

iso*Paraffins*

Curves of $-\Delta\sigma$ *v* $-\log_{10}\tau$ for seven *iso*paraffins are shown in Fig 8, and the other constants are given in Table V.

Neopentane, a highly symmetrical and relatively rigid molecule, owing to the close proximity of the four methyl groups, shows a positive configurational

entropy. The relatively mobile 2-methylhexane shows a highly negative entropy not very different from that of a *n*-paraffin. The configurational entropy of 2-methylpentane appears to be of the same order as that of *iso*butane and of *iso*pentane. Increased

TABLE V

*iso*Paraffin	η_B, cp	$\frac{\Delta H_p}{2{\cdot}3RT_B}$	$\frac{\Delta E_{vap.}}{T_B}$, E.U.	$\frac{\Delta H_p}{T_B}$, E.U.	$\frac{\Delta E_{vap.}}{\Delta H_p}$
*iso*Butane . .	0·245	1·325	18·91	6·06	3·12
*iso*Pentane . .	0·210	1·350	18·72	6·17	3·03
Neopentane . .	0·283	1·224	18·31	5·66	3·06
3-Methylpentane .	0·203	1·273	19·12	5·82	3·05
2,3-Dimethylbutane	0·231	1·311	18·95	6·00	3·16
2-Methylhexane .	0·198	1·408	19·58	6·43	3·04
2,2,4-Trimethyl-pentane . .	0·231	1·231	19·04	6·19	3·17

branching in 2,2,4-trimethylpentane and 2,3-dimethylbutane leads to a further lowering of the configurational entropy. In the former the central C-atom allows a certain amount of flexibility absent in the latter. The increased stiffening of molecules

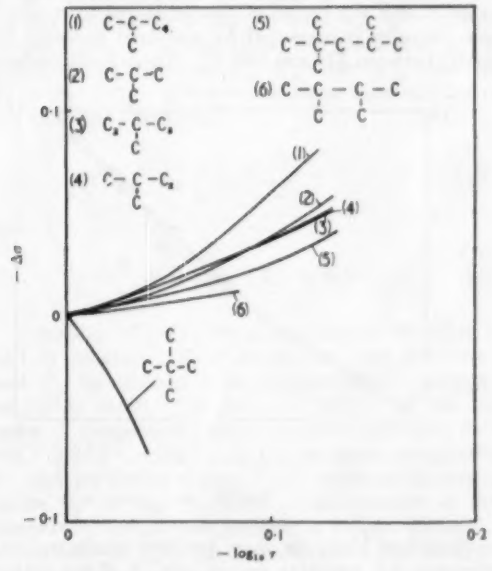

FIG 8

ENTROPY CURVE FOR SOME *ISO*PARAFFINS

thus leads to a decrease in the negativity of the configurational entropy, which may become even positive with very rigid molecules.

Aromatics

This group presents a picture similar to that of the *iso*paraffin, as can be seen from Fig 9 and Table VI.

Benzene, possessing a rigid structure, shows a

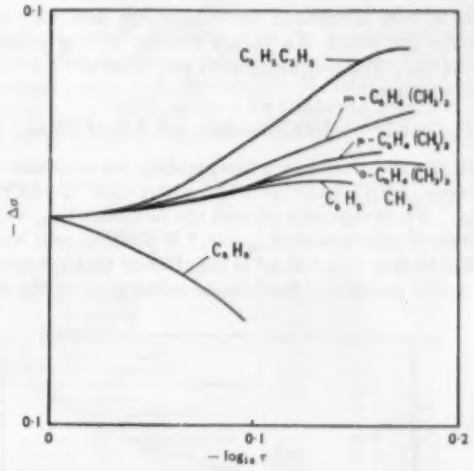

FIG 9

ENTROPY CURVES FOR SOME AROMATIC HYDROCARBONS

TABLE VI

Hydrocarbon	η_B, cp	$\frac{\Delta H_p}{2{\cdot}3RT_B}$	$\frac{\Delta E_{vap.}}{T_B}$, E.U.	$\frac{\Delta H_p}{T_B}$, E.U.	$\frac{\Delta E_{vap.}}{\Delta H_p}$
Benzene .	0·318	1·324	19·73	6·05	3·26
Toluene .	0·249	1·255	19·79	5·74	3·75
Ethylbenzene .	0·229	1·347	19·51	6·16	3·17
o-Xylene .	0·245	1·287	19·93	5·88	3·39
m-Xylene .	0·218	1·220	20·09	5·58	3·60
p-Xylene .	0·220	1·232	20·01	5·63	3·55

positive entropy, and the substitution of a methyl group in toluene renders the entropy slightly negative. The negative character of the entropy increases for ethylbenzene and gives intermediate values for the xylenes. Amongst the latter, the entropy increases in the order

ortho < *para* < *meta*

RESULTS BASED ON REFERENCE TEMPERATURES OTHER THAN THE BOILING POINT

For higher hydrocarbons the boiling point at atmospheric pressure may not be available, and it is necessary to choose a reference temperature without considering the equation of state of the liquid. In such instances equations (8) and (9) are applied. The data examined in the previous section have shown that in many instances $-\frac{c_p}{R}\log_{10}\tau$ is negative, and since the reference temperature T^*, which has to be chosen in the absence of values for the boiling point, usually corresponds to $\tau < 1$ ($\log_{10}\tau < 0$),

$$\frac{\Delta H_p^*}{2{\cdot}3RT^*} < \frac{\Delta H_p}{2{\cdot}3RT^*}$$

This is best illustrated by examining data for compounds for which the values for the boiling point is available. For *n*-octane, with 100° C as the reference temperature,

$$\Delta H_p/2{\cdot}3RT^* = 1{\cdot}48, \quad \text{whilst} \quad \Delta H_p^*/2{\cdot}3RT^* = 1{\cdot}32$$

with the same reference temperature for eicosane one obtains $\Delta H_p/2{\cdot}3RT^* = 2{\cdot}73$ whilst $\Delta H^*/2{\cdot}3RT^* = 2{\cdot}24$. From equation (9) and the fact that $\log_{10}\tau < 0$ one must conclude that $c_p + c_p^*$ is positive, and hence either that $c_p > c_p^*$ if c_p^* is negative or that c_p^* as well as c_p are positive. Both these cases arise in the two

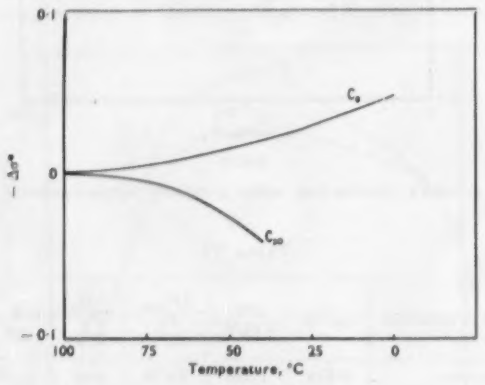

FIG 10

ENTROPY CURVES FOR *N*-OCTANE AND *N*-EICOSANE WITH 100° C AS REFERENCE TEMPERATURE

examples cited. If $-\Delta\sigma^*$ is calculated for *n*-octane and *n*-eicosane with $T^* = 373{\cdot}2°$ K (100° C), the values shown in Fig 10 are obtained. For *n*-octane, for which the reference temperature T^* is equivalent to $\tau = 0{\cdot}936$, $-\Delta\sigma^*$ is positive whilst for *n*-eicosane

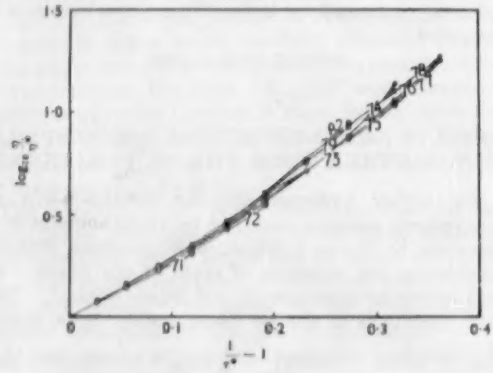

FIG 11

T^* is equivalent to $\tau = 0{\cdot}607$ $-\Delta\sigma^*$ is negative. The choice of the reference temperature can thus determine whether the entropy is positive or negative. In the two cases considered the reference temperature

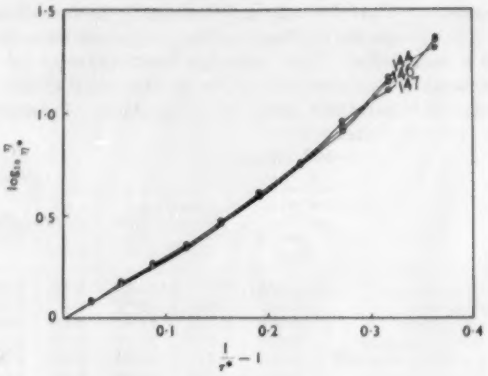

FIG 12

referred to different states of molecular flexibility. Whilst at 100° C molecules of *n*-octane are probably crumpled to a large extent, molecules of *n*-eicosane are, at the same temperature, extended, and the sign of the entropy of the latter is that of stiff molecules, namely positive.

The hydrocarbons present in lubricating oils have higher molecular weights and boiling points than *n*-eicosane, and the range of temperatures over which their viscosity is measured by standard methods lies usually between 37° and 100° C. These hydrocarbons

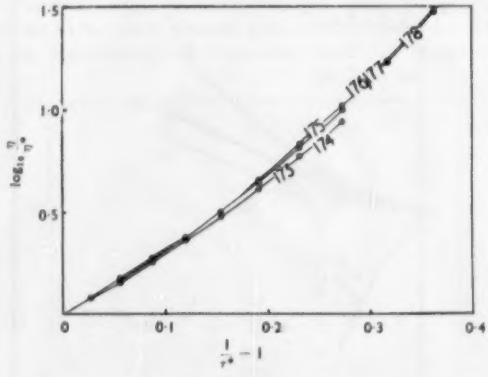

FIG 13

are therefore likely to show positive configurational entropies, *i.e.* negative values of C_p^*, if the highest temperature of measurement, say 100° C, is chosen as the reference temperature. This can be seen from Figs 11, 12, and 13, on which $\log_{10}\eta/\eta^*$ is plotted against $\left(\frac{1}{\tau^*} - 1\right)$, with $T^* = 373{\cdot}2°$ K (100° C) for a number of hydrocarbons in the range C_{25} to C_{27}. Fig 11 gives curves for the C_{26} alkanes. The numbers denoting the curves are those assigned to the compounds in the collection of data by Grunberg and Nissan [19] (71 : *n*-hexacosane; 72 : 3-ethyltetracosane; 73 to 76 : *n*-butyldocosanes; 77 : 78-*n*-amylhene-

icosanes; 79 : 11-(2,2-dimethyl-propyl)heneicosane; 82 : 5 : 14-di-*n*-butyloctadecane). Fig 12 shows curves for some *cyclo*pentanes (144 : *n*-(4-*n*-octyl)dodecyl*cyclo*-pentane; 146 : heneicos-11-yl*cyclo*pentane; 147 : *n*-(2-*n*-decyl)dodecyl*cyclo*pentane) and Fig 13 for a number of eicosyl*cyclo*hexanes.

It should be noted that all the curves bend upwards from the tangent through origin, and hence that the configurational entropies are positive.

A SIMPLE VISCOSITY–TEMPERATURE FUNCTION FOR HIGHER HYDROCARBON OILS

For hydrocarbon oils in the lubricating oil range, viscosity data are usually available only at a few selected temperatures, and if the viscosity–temperature relationships are to be expressed in terms of the equations proposed in the present paper a few simplifying assumptions must be made.

The results reported here make it clear that an equation using two constants (equation (1)) cannot express the variation of viscosity with the temperature, and the best one can do is to set up an equation with three constants, which require viscosity data at three temperatures. If these are available, the highest temperature can be used as the reference temperature. Suppose data are available at the absolute temperatures T_1, T_2, and T_3, and that $T_1 > T_2 > T_3$. If the temperature intervals are not too wide one can write

$$\log_{10} \frac{\eta_2}{\eta_1} = H\left(\frac{T_1}{T_2} - 1\right) \quad . \quad . \quad (10$$

and

$$\log \frac{\eta_3}{\eta_1} = H\left(\frac{T_1}{T_3} - 1\right) + K \log_{10} \frac{T_3}{T_1} \qquad (11)$$

Equation (11) is of the same form as equation (9), and in equation (10) it is assumed that between T_1 and T_2 the difference in configurational entropy is negligibly small. The factor H will be of the same order of magnitude as the more fundamental factor $\Delta H_p^*/2{\cdot}3RT^*$, with T_1 as the reference temperature T^* and the factor $K \log_{10} T_3/T_1$ replaces the entropy factor $C_p^*/R^* \log \tau^*$. From measurements at three temperatures it is thus possible to obtain the order of magnitude of the energy factor and the change in configurational entropy.

Calculations were carried out for a number of hydrocarbons in the range C_{25} to C_{27}, using viscosity data at 100°, 80°, and 60° C. Table VII gives the results of the calculations and also values for $\Delta H_p^*/2{\cdot}3RT^*$, with 100° C as the reference temperature.

n-Hexacosane in the range 60° to 100° C consists probably of fully extended and relatively rigid molecules, and the configurational entropy is positive. In 3-ethyltetracosane the presence of the substituted group restricts the alignment of the part of the chain and allows a certain degree of crumpling, and the entropy is hence negative. As the substituent group moves towards the centre of the chain in 7-*n*-butyldocosane and still further in 9- and 11-*n*-butyldocosane the chain stiffens by hindered rotation and the entropy factor becomes positive.

TABLE VII

No.	Hydrocarbon	$\Delta H_p^*/2{\cdot}3RT^*$	H	K	Sign of entropy
71	*n*-Hexacosane	2·473	2·518	−0·1765	+ ve
72	3-Ethyltetracosane	2·567	2·738	+0·0649	− ve
73	5-*n*-Butyldocosane	2·720	2·858	+0·0081	− ve
74	7-*n*-Butyldocosane	2·720	2·818	−0·0629	+ ve
75	9-*n*-Butyldocosane	2·620	2·664	−0·3672	+ ve
76	11-*n*-Butyldocosane	2·613	2·645	−0·5780	+ ve
77	11-*n*-Amylheneicosane	2·488	2·572	−0·4685	+ ve
78	11-Pent-3-ylheneicosane	2·527	2·594	−0·4685	+ ve
79	11-(2,2-Dimethylpropyl)heneicosane	2·670	2·762	−0·3550	+ ve
80	7-*n*-Hexyleicosane	2·650	2·780	+0·0609	− ve
82	5,14-Di-*n*-butyl-octadecane	2·805	2·957	+0·0081	− ve
120	9-*n*-Octylheptadecene-8	2·660	2·667	+0·1278	− ve
144	*n*-(4-*n*-Octyl)dodecyl*cyclo*pentane	2·900	3·065	+0·3630	− ve
146	Heneicos-11-yl*cyclo*pentane	2·820	2·997	+0·1197	− ve
147	*n*-(2-*n* decyl) dodecyl*cyclo*pentane	3·040	3·250	+0·7850	− ve
173	Eicos-2-yl*cyclo*hexane	2·870	2·786	−0·6370	+ ve
174	Eicos-3-yl*cyclo*hexane	2·970	2·978	−0·1015	+ ve
175	Eicos-4-yl*cyclo*hexane	3·060	3·121	−0·1013	+ ve
176	Eicos-5-yl*cyclo*hexane	3·100	3·104	−0·2720	+ ve
177	Eicos-7-yl*cyclo*hexane	3·140	3·223	−0·0385	+ ve
178	Eicos-9-yl*cyclo*hexane	3·140	3·186	−0·0609	+ ve
179	Heneicos-11-yl*cyclo*hexane	3·230	3·285	−0·0812	+ ve
180	*n*-Docosyl*cyclo*hexane	3·180	3·295	+0·3973	− ve

The same occurs in heneicos-11-yl*cyclo*pentane, whilst for *n*-docosyl*cyclo*pentane the entropy is negative.

DISCUSSION AND CONCLUSIONS

The investigation has shown that the change of the viscosity of hydrocarbons with the temperature is greatly affected by structural factors. The simple exponential equation, which in many instances can be used for simple liquids, requires modification when configurational changes are brought about by an increase in temperature. This is achieved by separating the free energy into two factors, and using a state of reference from which the entropy changes can be measured. The reference state most conveniently chosen is the boiling point at atmospheric pressure, at which it can be assumed that the degree of order at constant pressure is at a minimum. If this is done, then it is found that molecules which possess rigid structures give a positive configurational entropy, and hence that the free energy ΔE increases with decreasing temperature. Molecules possessing some internal freedom of rotation, and particularly those in which crumpling or coiling up of hydrocarbon chains is possible, give a negative entropy, indicating that the free energy decreases with increasing temperature. In *n*-paraffins at lower temperatures stiffening of the chain reduces the negative entropy, causing a change of the slope of the entropy curve, particularly with odd-numbered chains.

The reference state can be chosen at some arbitrary temperature without considering the equation of state of the liquid, but then it becomes more difficult to compare the results obtained for different hydro-

carbons. The principles outlined above, however, still apply.

Since the single exponential equation cannot be readily applied to hydrocarbons, it is suggested that an equation containing three constants may suffice for characterizing the viscosity–temperature relationship of hydrocarbon oils. The magnitude of the constants and their sign give an indication of the configurational changes which a change of temperature brings about in hydrocarbon oils.

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DISCUSSION

Prof. A. H. Nissan: The physical chemistry of hydrocarbon liquids appears, at first sight, relatively simple, particularly where saturated compounds are considered. A deeper insight, however, invariably shows that this first view is deceptive and that there are many interesting complications due to the multiplicity of forms and shapes which compounds of similar elementary composition, or even one and the same compound, can take. These secondary complications are fine in character and require tools of high resolution to detect them at first and study them afterwards. Such tools as spectroscopy in one of its manifold forms have been used effectively, but it is always a gain to knowledge that independent methods should be made available to measure and study these properties, particularly if the method is relatively simple in technique and apparatus. The measurement of viscosity is such a method—at least, it has become simple thanks to the continued efforts of the Institute of Petroleum and the ASTM in evolving standard though very accurate techniques. Mr Grunberg has now given us another key by which we can open a door and look in, as it were, on the hydrocarbon molecule to see how it appears and behaves in its most complicated state, namely the liquid state.

I have a few questions to ask, but before doing so would like to draw attention to one or two facts. In Fig 2 we see a plot which is reminiscent of a comet with a head in the left-hand bottom corner and a fine brush of a tail in the opposite one—what one may call the Grunberg Comet. When I first attempted this plot 15 years ago, data were not available to give all these details, and the curve that I obtained at the time was that shown in Figs 14 and 15. It will be noticed that the tail is missing simply because the viscosity at low temperatures for C_5, C_6, and C_7 was not available. Accordingly, I drew a mean curve and fitted an equation to represent this curve, the equation given as equation (7) in the paper. At the time I thought that this equation fitted the results for all members "above the first few" by which I meant the first four; I knew that it did not fit results for the lower members. Fig 2 shows that if C_5, C_6, and C_7 are omitted the equation still gives a tolerable representation of behaviour for the rest of the *n*-paraffins. In other words, the equation fits members above C_8 instead of C_5. I am drawing attention to this fact, not because I want to justify equation (7) in any sense, but to illustrate another side of the picture that we are discussing tonight. In the paper, Mr Grunberg is concerned with a study of the fine differences between

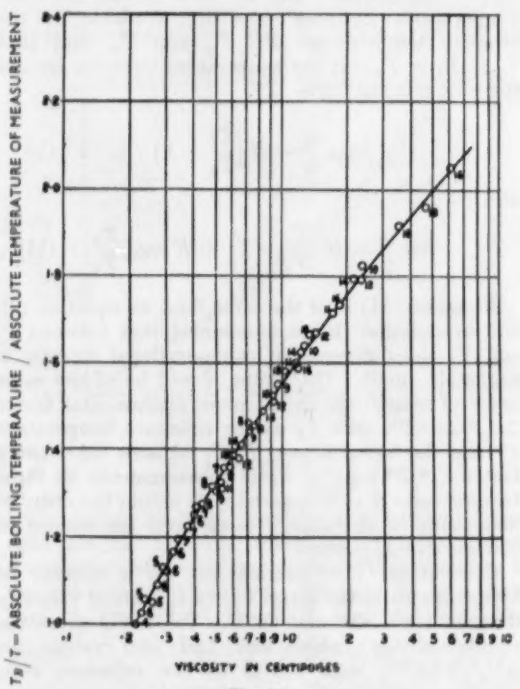

FIG 14

members of each series and between members of different series. Equally interesting is a study of the similarities obtained. Thus, it is a notable fact that even with the more accurate data, members of the *n*-paraffin series from C_9 upwards to C_{100} give an almost identical curve

when plotted in this manner. More than that, Mr Grunberg and I have extended this plot up to the critical point as shown in Fig 16. Again it is seen that at the saturation pressure the liquids give a remarkably close concentration of points. Finally, it is equally interesting to observe that in going beyond the critical point into the gaseous regime and down again in temperature, we obtain, once again, a very close approximation to a single curve. In studying the differences that exist we must not lose sight of the fact that there is still a lot to be done in explaining the similarities which are observed. I would like to ask Mr Grunberg three specific questions on this side of the picture:

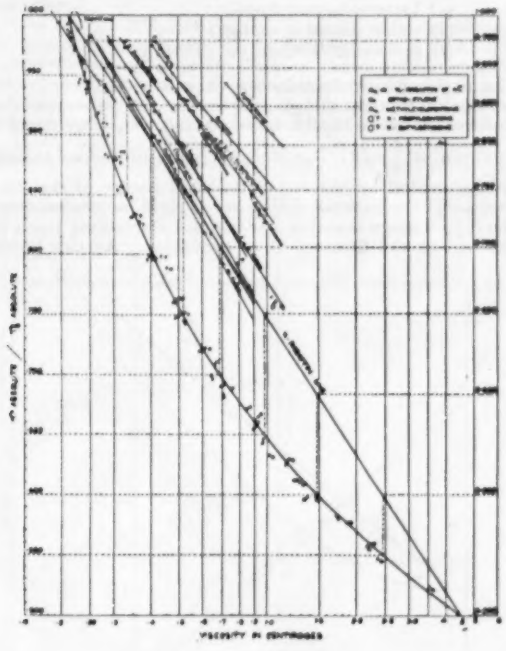

FIG 15

(1) Has the new API work materially affected the picture in its broad rather than its detailed aspect of the similarity of the behaviour of this vast number of compounds when plotted against T/T_B?

(2) Would he say a few words about what he thinks to be the reason why the molecules in the vapour state give us this similarity?

(3) He will no doubt remember that we have connected the vapour with the liquid viscosities by the following equation at equal values of T/T_B.

$$\log \mu_{sat.\,vap.} = -4{\cdot}6965 - 0{\cdot}2040 \log \mu_{sat.\,liq.}$$

Would he care to let us have his views about the significance of such an equation in terms of the internal energy and entropy of the molecules?

It will be thought that I have strayed away from the paper in asking these questions, but I hope it will be agreed that it is necessary not to forget the broad similarities which exist when we are engaged in studying fine differences. Coming to the differences themselves, I would like to ask Mr Grunberg to amplify one or two points. Referring to equation (5), can Mr Grunberg let us know in a little more detail how $C_{p'}$ which is a specific heat factor and not the specific heat of the liquid, correlates with the measured specific heats of these liquids at different temperatures? The reason I ask for this is, I believe, evident in that if we can have an explicit relationship between this factor and specific heat of liquids at constant pressure we shall then be able to compare the results of viscometric studies with those of specific heat measurements and confirm our picture of molecular behaviour or otherwise find differences in our views of their shapes and configurations. It will also make it possible to visualize more explicitly the significance of a negative $C_{p'}$.

My next question is again a request for amplification. Both for neopentane and benzene we have an entropy change which, if my understanding of the paper is correct, shows that there is a decrease of entropy of configuration with rise in temperature or, in the terminology of the paper, an increase with a drop in temperature. Can the author clarify the physical picture of how this state of affairs can be envisaged, since it appears to be a general rule for the so-called rigid structures?

Finally, I would like to refer to the section dealing with reference temperatures other than the boiling point. I am sorry to see that the sign of the entropy term is so arbitrary and depends in such a fortuitous manner on the choice of the temperature which is made. As Mr Grunberg explained, this is entirely due to the fact shown in equation (9) that ΔH_p^* has really a little bit of entropy term in it, and this appears to upset the "apple cart." I would like to ask Mr Grunberg if he had estimated the internal energy terms as well as the entropy term more directly than was done in the paper, would he have obtained a more definite result? By this I mean that if we first of all determined ΔE_{vis} from the viscosity curve at different temperatures, then plotted this term against the temperature, and once again differentiated with respect to temperature, we would, of course, have got definite values for the internal energy and the entropy terms making up ΔE_{vis}. Such a method is long and tedious and suffers from the errors of two graphical differentiations, but would it give us absolute values for the terms we are trying to evaluate? Furthermore, would such a method be more revealing than the present

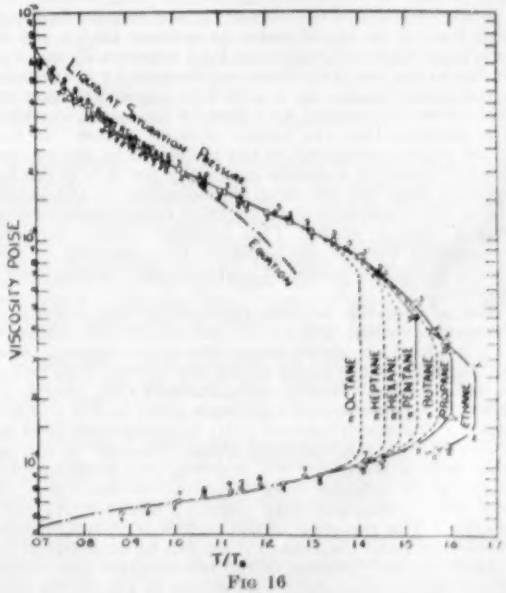

FIG 16

one in indicating explicitly whether ΔH_g is truly invariant with temperature or whether it is somewhat dependent on the temperature at which we measure our values because we are working at constant pressure rather than at constant specific volumes? Finally, if ΔH_g were to be found temperature dependent, would it be possible to subtract from it a term for $(P\Delta V)$ and obtain a temperature-invariant ΔH?

L. Grunberg: I must start my reply with a disclaimer: my own contribution to Fig 2 was only of a minor character, since the method of plotting had been worked out by Professor Nissan and the data had been provided by the API. An appropriate name for the figure would therefore be the "API galaxy," in which the "Nissan constellation" shines prominently. His contention that this method of plotting brings out similarities in behaviour of various hydrocarbons is perfectly correct. The present paper has attempted to show that within the framework of that method it is also possible to interpret differences in behaviour. The paper also shows that the new API data have not materially affected the correlation of viscosity on the basis of T/T_g, *i.e.* τ. Figs 14 and 15 illustrate the small number of data on which the original correlation was based, and it is gratifying to note that the latter has not been upset by the large amount of data produced by the API.

Professor Nissan has mentioned our extension of the correlation to temperatures between the boiling point and the critical temperature, as shown in Fig 16. The reason for the good correlation is probably owing to the fact that the shape of the *n*-paraffin chains does not change over this range. The "crumpling" of the chains is almost completed at the boiling point, as indicated by the constancy of the ratio of $\Delta E_{vap}/H_g$ at this point. It is perhaps important to mention that equation (7) is not applicable to values of $\tau > 1$ as indicated by the line marked "equation" in Fig 16. Equation (7) represents the first members of an infinite series in increasing powers of τ, which converges only for $\tau < 1$.

The correlation of the viscosity of the saturated vapour with that of the liquid seems to indicate that a law of rectilinear diameters exists for $\log \eta_l$ between T_g and T_c, similar to the law of Cailletet and Mathias for the density *v.* the temperature. It is therefore possible to give an explanation by analogy with that for the latter, in which it is assumed that the vacant sites or "holes" in the liquid phase correspond to the molecules in the vapour phase. Since $\log \eta_l$ stands essentially for ΔE, it can be assumed that the ΔE-term characteristic of the liquid phase, has a corresponding negative term, characteristic of the vapour phase. This negative energy term is responsible for the deviation of the viscosity of the vapour from that predicted by the simple kinetic theory of gases.

The relationship between the specific heat factor and the normal specific heat is best understood with reference to Fig 17, which shows these data for *n*-hexane. The bottom part of the figure shows the specific heat factor as derived from viscosity data, marked $C(\eta_l)$, similar to those for *n*-pentane and *n*-eicosane given in Fig 6 of the paper. The curve marked $C(H)$ is the specific heat as observed from heat capacity measurements. It can be seen that between $\tau = 0{\cdot}5$ and $0{\cdot}6$, $C(\eta_l)$ rises steeply, whilst $C(H)$ changes only slightly. Between $\tau = 0{\cdot}6$ and $0{\cdot}9$ $C(\eta_l)$ changes only slightly, whilst $C(H)$ rises rapidly. The variation of the factors is therefore complementary, and the sum of these can be expected to be a much simpler function of the temperature than either of the factors separately. As shown in Fig 17 the sum $[C(\eta_l) + C(H)]$ gives a straight line when plotted against τ. For *n*-hexane

$$C(\eta_l) + C(H) = 20\tau + 30 \text{ cal. mol}^{-1} \text{ degree}^{-1}$$

In order to discuss the change in the sign of the specific heat factor referred to by Professor Nissan it is necessary to recapitulate briefly the main factors which determine the change of viscosity with the temperature. These are:

(*a*) intermolecular forces;
(*b*) order–disorder changes;
(*c*) molecular flexibility.

The way in which these factors express themselves in the particular representation adopted in the paper can be understood from Fig 17, in which $\log \eta_l - \eta_g$ is given as a function of $\frac{1}{\tau} = 1$. The melting point of the substance is represented by the top right-hand corner of the diagram. If the substance consists of rigid molecules, then the liquid range is rather narrow and the boiling point is reached at the first set of co-ordinates. At this point

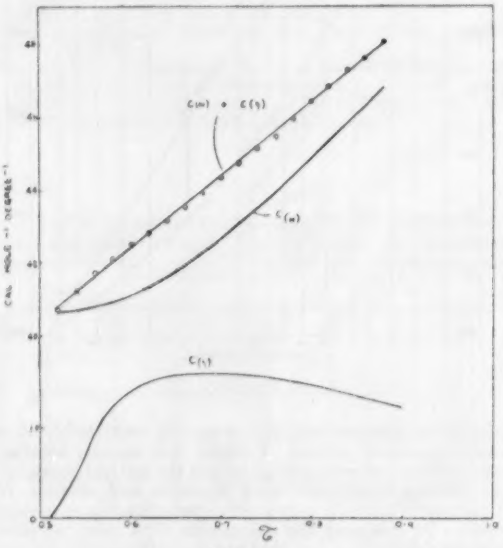

FIG 17

the tangent through the origin lies below the curve, and the difference between the straight line and the curve is negative leading to a negative specific heat factor. This is due to changes in the intermolecular forces and in the degree of order. With flexible molecules, the liquid range is increased and the co-ordinates are displaced to the left and downwards until a stage is reached where the tangent through the origin lies above the curve and the difference between the straight line and the curve is positive, giving a positive specific heat factor. The flexibility of the molecules swamps the effects of the intermolecular forces and the degree of order.

The method of evaluating the entropy changes illustrated in Fig 18 is preferable to the method of double differentiation suggested by Professor Nissan. I have tried the latter method and found it a rather coarse tool for the investigation of fine differences. Fig 18 also provides an answer to the supposed arbitrariness of the sign of the entropy when using a reference temperature other than the boiling point. Choosing a lower reference temperature is equivalent to moving the co-ordinates upwards and to the right. If the reference temperature is very much lower than the boiling point the co-ordinates may be shifted to a range in which the flexibility of the molecules is reduced and the sign of the entropy is reversed. This is well illustrated in the paper for *n*-

eicosane with 100° C as the reference temperature. Thus, whilst the choice of the reference temperature may be arbitrary, the result obtained is not, since it refers to the particular state of the liquid in the range of temperatures considered.

The energy ΔH_p does not vary with the temperature, since it is the free energy at the boiling point. It would, however, be useful to investigate the negative specific heat factor of rigid molecules in relation to the change of volume. This is not at all easy, since the change in volume would have to be divided into a part associated with the change of intermolecular distances (causing a change of the intermolecular forces) and a part involving

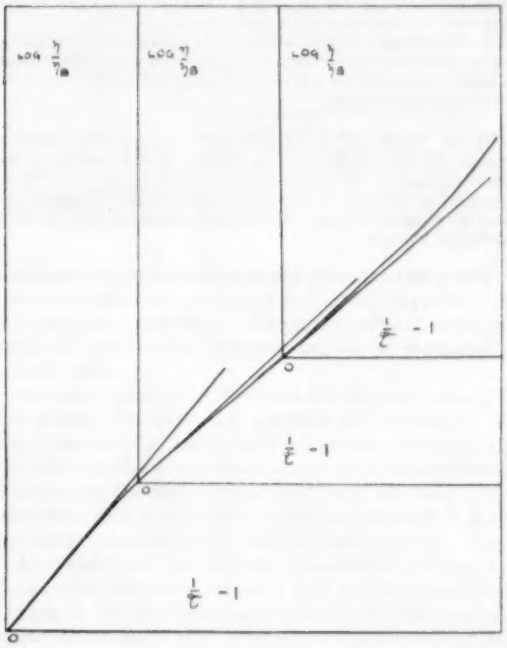

FIG 18

the change in the number of unoccupied sites or "holes" (connected with the change in the degree of order of the molecules in the liquid).

Dr R. J. Russell: I would like to ask Mr Grunberg a question concerning negative entropy. It appeared to me that in the whole paper this was the most difficult thing to understand, and it appears that Professor Nissan agrees with me. From Mr Grunberg's argument, it also appears that the derivation of the activation energy assumed that at the boiling point and close to the boiling point, there is no change of order in the liquid. I should have thought that if a change of order was assumed a larger activation energy would be obtained and the necessity for a negative entropy would probably disappear. The change in the shape of the entropy curve with change in reference temperature might also be avoided. I would like to know if Mr Grunberg has considered this possibility.

L. Grunberg: I think Fig 18 amply illustrates how the negative sign arises. The change of order which arises at the boiling point is that of a complete change of phase during the process of vaporization. The only possible assumption which can be made is that the slope of the tangent to the curve at the origin is a measure of the free energy of activation at the boiling point.

Dr R. J. Russell: I take it that by using the tangent at the origin, the assumption is that there is no change in ΔS near the point where the activation energy is derived. If this is not so, the activation energy could be larger.

L. Grunberg: There can be no change of ΔS at the reference temperature at which the energy is derived, since the change in ΔS is taken as the difference between the entropy term at any one temperature and that at the reference temperature. The free energy of activation at the reference temperature cannot be greater than that obtained by the method used in the paper.

G. H. Thornley: I was interested to hear Professor Nissan say that the hydrocarbon molecules are not really as dead as the text books would have us believe. That recalls to my mind a statement by Ricardo many years ago, in a paper on diesel engines. He referred to their lubrication systems, whereby the crankshaft bearings and, through a drilled connecting rod, even the small end bearings are lubricated by oil which has to get there by registering with a hole in the main crankpins, and, for the small ends, in the big end crankpins as well. He said it was rather odd that the oil, after slumbering in the bosom of Mother Nature for millions of years should still have the agility to leap aboard.

On the question of stretched molecules, which become coiled, I think Mr Grunberg indicated that they become coiled as they approach boiling point. At a recent meeting of the London Branch, some explanation of the mechanism of the behaviour of viscosity index improvers was being sought, and different opinions were expressed. One view, which did not seem to receive universal acceptance at the meeting, was that the long chain molecules of the high polymers are, I think, stretched and long at low temperatures, and become coiled as the temperature increases. Just in what way that would explain how we get a lesser increase in viscosity at low temperatures than we would have expected, and a greater increase in viscosity at high temperatures, I do not quite know. I am sure Mr Grunberg will tell us that it is either all nonsense or capable of a clear explanation.

L. Grunberg: I believe there may be something in the argument that the molecules of V.I. improvers change their shape with the temperature, much in the same way as the molecules of simple hydrocarbons which we have been discussing. The situation in oils containing V.I. improvers is complicated by the large size of the polymer molecules and the fact that probably two separate phases are present. One then deals with colloidal systems, not amenable to simple interpretations.

W. Barker: Does the fact of the chains crumpling up, as you put it, affect the Newtonian properties of hydrocarbons?

L. Grunberg: There have been suggestions that hydrocarbon liquids consisting of elongated molecules would show non-Newtonian behaviour at very high rates of shear, owing to the tendency of the molecules to orientate themselves in the direction of flow. If this situation arises, then the "crumpling" of hydrocarbon chains would shift the point at which non-Newtonian behaviour could occur to higher temperatures. This shift would also manifest itself independently of the shape of the molecules, since it has been suggested that non-Newtonian behaviour of ordinary liquids may set in when the rate of shear approaches values of the order of the thermal velocity of the molecules divided by the intermolecular distance. The order of magnitude of the rate of shear

at which non-Newtonian behaviour may be possible would be about 10^7 sec^{-1}.

Prof. A. H. Nissan: When dealing with ultrasonics it is necessary to remember that what is called the second coefficient of viscosity may be taking part. A discussion on the phenomena associated with the second coefficient of viscosity and with phenomena observed when liquids are irradiated by ultrasonics took place at the Royal Society either in 1953 or 1954 and appeared in their *Proceedings*.

Dr A. S. Freeborn: I should like to ask Mr Grunberg whether he can tell us anything more about crystallization in liquid hydrocarbons. Is it possible to say what percentage of the molecules are "crystallized" in the liquid?

L. Grunberg: When talking about the degree of order in a liquid or its "crystallinity" one must avoid thinking in terms of well-defined crystallites floating in an otherwise uniform medium. The ordered structures are transitory and change in time as well as in space. There exists a dynamic equilibrium between the ordered and the disordered regions of the liquid. It is difficult to give a definite figure for the extent to which the ordered arrangement of the molecules in the crystal are preserved after melting. The increase of volume during melting is only of the order of 10 to 15 per cent, and such a small increase in volume can be associated only with a relatively small disarrangement of molecules.

In the particular case of water, it is possible to assess the extent to which the order is preserved after melting. This is done by estimating the percentage of unbroken hydrogen bonds, since in the disordered regions only van der Waal's forces would exist. Professor Nissan and I have calculated that between 70 and 80 per cent of the hydrogen bonds are preserved after melting. Similar calculations cannot be made for hydrocarbons, since the same type of forces exist in the ordered and disordered arrangements.

Dr A. S. Freeborn: Is that an indication of the fact that the bond is not anything like as strong as in water?

L. Grunberg: Yes, that is right. In hydrocarbons the intermolecular forces are all of the van der Waal's type, whilst in water one also has hydrogen bonds, which are very much stronger.

G. H. Thornley: It is now my very pleasant duty to thank Mr Grunberg for his paper. I am sure you will agree with me that the thanks of all of us who are interested in petroleum are due to people like Mr Grunberg and Professor Nissan, who apply their minds to these abstruse things.

The vote of thanks was accorded with acclamation.

DESULPHURIZATION OF GAS OILS BY CATALYTIC HYDROGENATION *

By W. C. VAN ZIJLL LANGHOUT,† G. J. F. STIJNTJES,† and H. I. WATERMAN †

(with the collaboration of C. BOELHOUWER † and W. C. DE RHOTER †)

SUMMARY

The significance of desulphurization in the petroleum industry is discussed, and a review is given of some important industrial hydrodesulphurization processes. Thermodynamic calculations of the possibility of desulphurization and dehydrogenation reactions in distinct simplified systems (mixtures of equimolecular amounts of methyl thiophene, methyl*cyclo*hexane and hydrogen) show, that in the equilibrium, at a certain temperature, a total pressure can be calculated at which no production or consumption of hydrogen occurs. This forms the base of the so-called " Autofining " process, in which mineral oils are desulphurized by hydrogenation, whilst the necessary hydrogen is obtained by dehydrogenation of the naphthenes in the feed.

A description is given of desulphurization experiments on Middle East gas oils in the gas phase, using a Co–Mo–Al_2O_3–catalyst. At a constant temperature (375° C) and contact time (9 sec), the influence of pressure and W.H.S.V. (weight hourly space velocity) were investigated. Pressure increase (26–91 atm abs) improved desulphurization of the oils, increase of the W.H.S.V. (1·5–5·4 kg feed per l of catalyst per hr) showed the opposite effect. The catalyst was very selective : hydrogenation of the aromatics took place to a small extent only at higher pressures (approx 150 atm). Cracking was of no importance under the conditions of the experiments.

DESULPHURIZATION of mineral oils and the products derived therefrom nowadays is of great importance to the petroleum industry. The production of crude oils with a high-sulphur content has been increased in recent years.

Sulphur removal in the past was applied mostly to low-boiling fractions, *e.g.* gasoline and kerosine. By the " sweetening " of these fractions the corrosive and malodorous thiols are transformed into dithioalkanes. To increase the lead susceptibility and also to prevent the formation of corrosive oxidation products it is desirable to remove all the sulphur compounds.

In diesel fuels the sulphur compounds have an unfavourable influence on wear and engine cleanliness. Owing to the increasing number of catalytic cracking units the production of cycle oils is also increasing, and these oils are often used for blending purposes for the production of diesel fuels. Generally, the cycle oils have a high sulphur content. Therefore the desulphurization of higher boiling petroleum products, *e.g.* diesel fuels, has become more necessary. In most cases, the conventional processes cannot be applied to the desulphurization of the heavier fractions.

One of the reasons for this is that the sulphur compounds of the higher boiling fractions are generally of the non-reactive cyclic type, whereas thiols are absent or present only in very small quantities.

Generally, the sulphur content of the heavier oil fractions is higher than that of gasoline and kerosine.

Desulphurization therefore causes a large loss of chemicals, whilst also other specific difficulties have to be conquered. Moreover, there is a considerable loss because the sulphur compounds are removed as such, for instance in the solvent extraction processes, and there is not yet a wide field of application for the sulphur concentrates.

In recent years, many oil concerns have studied catalytic hydrodesulphurization on a laboratory scale and also in pilot plants. From the high-pressure technique applications in the field of preparation of liquid fuel from coal and brown coal, and also from the catalytic transformation of heavy oil residues into lighter fractions, it was known that there was very considerable desulphurization. This knowledge, however, could not be applied for the development of an economically justified catalytic hydrodesulphurization process. The reasons were the high capital investment for the high-pressure equipment, the considerable consumption of hydrogen, the necessary energy for the recycling and heating of the hydrogen, and the cost of the catalyst.

Furthermore, saturation of aromatics and excessive cracking were undesirable side reactions. By the study of several catalytic reforming processes a thorough knowledge of dehydrogenation of naphthenes was obtained. In many reforming processes the chief reaction was the formation of aromatics by dehydrogenation. A principal way of producing hydrogen was thus available. The British Petroleum Co. Ltd. (Anglo Iranian Oil Co. Ltd.) has developed a process named " Autofining," in which the hydrogen which is necessary for the desulphurization is produced simultaneously by the dehydrogenation of the naphthenes present in the feed.[1]

The energy consumption and the capital investment for the recirculation and the reheating of the hydrogen have to be minimized. It is even possible to reduce the quantity of hydrogen below the quantity which is necessary to keep the oil in the vapour phase. The process in which this possibility is realized has been developed by the Royal Dutch/Shell group.[2,3] It involves the application of the " trickle " technique, a large proportion of the oil being in the liquid phase.

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The catalyst ought to be cheap and mechanically strong; in many cases the catalyst should have a certain selectivity towards the desulphurization of the sulphur compounds.

In the present paper, a survey is given of the research work which has been done in the field of catalytic hydrodesulphurization, chiefly of heavy oils.

The oil, together with hydrogen, passes through a catalyst; hydrogen sulphide and hydrocarbons are formed. Afterwards, the desulphurized oil has to be separated from the hydrogen.

Catalysts are generally metal oxides or sulphides of the elements of the sixth or eighth group of the periodic system, supported or non-supported.

In the research work of the Union Oil Co. of California [4] for the catalytic desulphurization of gasolines, experiments were carried out for instance with catalysts consisting of CoO and MoO_3, deposited on bentonite. It was proved that the CoO–bentonite and MoO_3–bentonite catalysts were less active than a catalyst consisting of a physical mixture of CoO and MoO_3 on bentonite as a carrier. The activity of the latter was greatly surpassed by a catalyst composed of a chemical compound, cobalt molybdate ($CoMoO_4$), and bentonite as a carrier.

Hoog [5] and collaborators also studied catalysts which were prepared from the oxides of cobalt and molybdenum on supports, *e.g.* aluminium oxide and bauxite. The proportion of Co to Mo and its relation to the activity of the catalyst in hydrodesulphurization were taken into consideration. The catalyst with the highest activity contained less cobalt than molybdenum (atomic proportion Co–Mo equal to 1 : 5). The catalyst life was long. Hydrogenation experiments with this type of catalyst, working with pure sulphur compounds in sulphur-free paraffinic oil, showed that there was hardly any cracking and hydrogenation of the aromatics.

A mixture of cobalt and molybdenum oxide, a compound containing cobalt, molybdenum, and oxygen or a mixture of the oxides with the compound on supports, such as bauxite and aluminium oxide, are mentioned as catalyst for this process.[1–3, 7, 8, 10–16] Catalysts, such as tungsten nickel sulphide [17] and molybdenum sulphide [18] when compared with the catalysts mentioned above, show certain disadvantages, chiefly in connexion with the desired selectivity.

Nickel oxide on supports, for instance kieselguhr,[19, 20] may have a sulphur-alkene selectivity, *i.e.* desulphurization of the oil occurs without any hydrogenation of the alkenes. The addition of alkali salts to catalysts of the oxide type on supports, such as aluminium oxide and bauxite, might also prevent the hydrogenation of the alkenes in the hydrodesulphurization process.[33] Other proposed catalysts are, for instance, Fe, Ni, or Co oxides supported by aluminium oxide and kieselguhr [21] and aluminium oxide and molybdenum oxide on Al_2O_3.[9] The mechanism of the desulphurization has been studied among others by Hoog.[34] In this investigation Middle East gas oils were treated in gas phase at 375° C and pressures of 11 to 51 atm abs with hydrogen in the presence of a Co–Mo–aluminium oxide catalyst.

Three of the processes which are suitable for the desulphurization of higher boiling oil fractions and which have reached the commercial stage are discharged here, namely the "Autofining" process of the British Petroleum Co. Ltd.; the cobalt molybdate process of the Union Oil Co. of California; and the "trickle" process of the Royal Dutch/Shell group.

The "Autofining" process of the British Petroleum Co. Ltd.[1, 19, 27] can be defined as a desulphurization process for petroleum distillates by catalytic hydrogenation, in which the sulphur compounds are transformed with hydrogen into hydrogen sulphide and hydrocarbons. The hydrogen was obtained by dehydrogenation of the naphthenes present in the feed. The oil, together with gas containing hydrogen, is passed over the catalyst; desulphurization and dehydrogenation occur. After cooling the gas and the liquid are separated and the gas recirculated. The hydrogen sulphide is not removed from the circulating gas. The hydrogen sulphide, which is dissolved in the liquid and which is in equilibrium with the hydrogen sulphide in the gas, is regularly carried away by the reaction product. The majority of the oils can be economically desulphurized by this process. The reaction conditions are as follows: [1]

Pressure	5–15 atm
Temperature . . .	400°–430° C
Velocity of feed (L.H.S.V.)	1–5 litres of oil (0° C)/litre of catalyst/hr
Gas rate	350–700 litres of hydrogen (0° and 1 atm)/litre of oil (0° C)

The dehydrogenation of the naphthenes to aromatics is enhanced by the increase of temperature; the increase of pressure decreases the production of hydrogen. Desulphurization is promoted by the application of high hydrogen partial pressures. For practically all oils the temperature of about 410° C gives the best desulphurization. Above 430° C the product becomes strongly aromatic, and there is also considerable cracking, which is undesirable for the quality of the product. Moreover, if too high temperatures are applied, by the covering of the catalyst with carbon-rich products, the activity is lost more rapidly.[22]

Higher boiling oil fractions, such as gas oil, generally contain more sulphur and also have a more narrow range of temperature and pressure which facilitates economic desulphurization. Naphtha and kerosine behave differently in this respect. By the use of oil fractions (gas oils) with a wide boiling range this difficulty can be partly avoided. The hydrogen which is liberated by the dehydrogenation of the naphthenes from the lower fractions reacts with the sulphur compounds from the higher fractions.[30, 31] The L.H.S.V. (litres of oil (0° C) per litre of catalyst per hour) is a factor of economic importance. With naphtha and kerosine, higher feed rates can be applied (5–l/l/h); for the heavier sulphur-rich oil fractions the L.H.S.V. may not be higher than 1–l/l/h. Otherwise the

desulphurization of the heavy oils becomes too low. The gas rate (litres of hydrogen (0° C and 1 atm) per litre of oil) has not a very great influence on the degree of desulphurization, and therefore should be kept as low as possible, and this also results in a saving in energy costs. After a relatively short time the catalyst loses its activity (about 1000 hr for naphtha and kerosine and about 200 hr for gas oil). Regeneration is done *in situ* by steam–air or inert gas–air mixtures.

At the beginning of the first period the catalyst is less active,[1, 22] but after a part of the catalyst has been sulphidized during the process or by a pretreatment with gases containing hydrogen sulphide, the maximum activity is reached. The overall heat of reaction is practically zero, the heat liberated by the desulphurization reactions being balanced by the loss of heat by the dehydrogenation of the naphthenes. Naphtha and kerosine in this process are almost completely desulphurized.[24, 25, 26] The sulphur removal from gas oil is 50 to 70 per cent, depending on the L.H.S.V.,[1, 28] whilst oil residues are much more difficult to desulphurize [22] by this process.

Of more recent date are the investigations of the British Petroleum Co. Ltd., in which a gas oil was more than 40 per cent desulphurized at 427° C, 50 atm and a liquid hourly space velocity of 5 litres of oil/litre of catalyst/hr. The catalyst was of the Co–Mo–aluminium oxide type. Recirculation of hydrogen was not applied in this case, the greater part of the oil passing in the liquid phase over the catalyst;[32] the hydrogen of the dehydrogenation is used for the desulphurization reactions.

The " trickle " process of the Shell Group [2, 3] seems to give savings of 15 to 20 per cent for the capital investment compared with the analogous gas phase process.[34] Working in the gas phase the recirculation of hydrogen must be high enough to ensure that all the oil can be brought into the vapour phase. This condition is not necessary in the " trickle " process. The oil flows in a thin film down the reactor over a solid catalyst bed.[2, 3, 35–37] This enables a low hydrogen circulation to be used. The result is a decrease in the energy consumption of the recycle hydrogen compressors. A reduction in the heat transfer surface area is also possible in this process, for a much smaller amount of heat has to be transferred.

Gas oils and cycle oils (obtained in catalytic cracking) with a high sulphur content are desulphurized to the extent of 85 to 90 per cent; the cetane number of the cycle oil increases. After desulphurization the cycle oils are extremely useful as a feed for catalytic cracking. Furthermore, by the decomposition of the sulphur compounds in the desulphurization process gasoline with a high aromatic content is formed. The hydrogen sulphide formed during the process may be used for the sulphur production. The conditions of the process for the treatment of, for example, a light catalytically cracked cycle oil, with a boiling range of 240° to 340° C and a sulphur content of 3·1 per cent weight, are as follows:

Pressure	50 atm
Temperature	375° C
L.H.S.V.	1·1 litres of oil (0° C)/ litre of catalyst/hr
Gas rate	250 litres of hydrogen (0° C and 1 atm)/ litre of oil

Under these conditions a desulphurization of 94 per cent may be obtained in the example given.

The maximum desulphurization was obtained when the hydrogen recirculation was such that only the transition conditions (break point) of the " trickle " and the gas phase process occur. If, at a given L.H.S.V., pressure, and temperature, the hydrogen rate is increased, so that the gas phase process starts, the desulphurization decreases as a result of the decrease of the contact time and the lower oil vapour partial pressure. At gas rates below the break point the desulphurization decreases, which is probably caused by the lower mass-transfer rate in connexion with the resistance of the liquid film on the catalyst surface. At a very low hydrogen recycle rate the decrease in desulphurization will be caused by the lower hydrogen partial pressure existing in the lower part of the reactor (downstream).[2, 3]

The influence of hydrogen sulphide in the recirculation gas on desulphurization is generally so small that removal of hydrogen sulphide is not necessary. Light hydrocarbons in the recirculation gas have a small but distinct influence on desulphurization. If oils with a high percentage of sulphur are to be treated, the quantity of hydrogen consumed may be so large that the light hydrocarbons have to be removed from the gas.

In this process the aromatics are hardly hydrogenated at all, but the hydrogenation of the alkenes cannot be avoided. A very high pressure (150 atm) is necessary to remove the nitrogen compounds, for instance from shale oil.

The low decrease of activity of the Co–Mo–bauxite catalyst is very important; the catalyst life is of the order of one year. The reactor is subdivided into a number of catalyst beds,[2, 24, 39] between which a part of the cold charge oil can be introduced. Thus, the excess of heat of the exothermic desulphurization reaction can be removed. The number and the height of the catalyst beds required depend upon the sulphur content of the feed and upon the degree of desulphurization desired. In the processing of oils poor in sulphur there is no necessity to introduce oil between the catalyst beds.

The cobalt molybdate process of the Union Oil Co. of California (" unifining ") does not differ much in principle from the " Autofining " process,[7] only in this case hydrogen is used from the outside, which is different from the process of the British Petroleum Co. Ltd. In " unifining " no heat from the outside is necessary. The temperature at which the oil feed enters the reactor depends on the sulphur content and the degree of unsaturation of the oil. Above 260° C the hydrogen reactions start, as a result of which the temperature

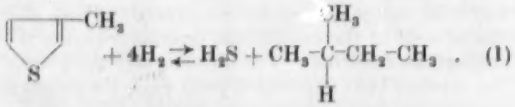
may rise to 340° C. Above this temperature the desulphurization starts. In this process, too, the aromatics are hardly hydrogenated. Cracking cannot be completely avoided. The conditions for this process can be illustrated by an example which refers to an oil with a boiling range of 80° to 500° C and a sulphur content of 3·5 per cent weight.

Average bed temperature	450° C
Reactor pressure . .	110 atm
L.H.S.V. (liquid hourly space velocity . . .	3·2 litres of oil (0° C)/litre of catalyst/hr
Hydrogen consumption .	200 litres of hydrogen (0° C, 1 atm)/litre of oil (0° C)
Desulphurization . .	99 per cent

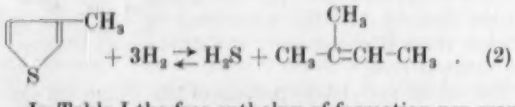
The catalyst life is short, *e.g.* 150 hr. Regeneration is therefore always necessary. To avoid this drawback a continuous process has been developed by the Union Oil Co. of California. This process, named "hyperforming,"[40] is based on almost the same principles as the T.C.C. (Thermofor Catalytic Cracking) processes. The catalyst is brought to the top of the reactor and then proceeds downflow and in countercurrent with the oil. The catalyst which leaves the reactor is then brought to the regenerator, in which the deposit of coke is removed by controlled oxidation of the carbon. The combination of a moving bed in the regenerator, together with controlled oxygen content in the flue gases, limits the temperature rise.

THERMODYNAMICAL CALCULATIONS OF DESULPHURIZATION REACTIONS

Thermodynamic constants of different sulphur compounds have been published. No data, or only a very few, are available for the cyclic compounds of the benzothiophene and dibenzothiophene types. Precisely these compounds are present in higher boiling oil fractions. Therefore, for the study of desulphurization the hydrogenation of 3-methylthiophene has been studied. It has been proved that for the reactions (1) and (2) below 800° K the equilibrium lies practically to the right side, *i.e.* the hydrogen sulphide and alkane or alkene.



(1)



(2)

In Table I the free enthalpy of formation per gram-molecule of the different compounds are given. The calculated equilibrium constants are found in Tables II and III. Increases of the total pressure will promote desulphurization.

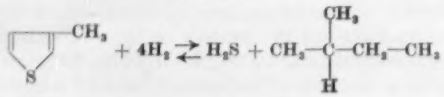
If, besides the desulphurization reaction, naphthene dehydrogenation (reaction 3, Table IV) is also studied, then at a definite temperature, and starting with one gram-molecule of 3-methylthiophene, one gram-molecule of methyl*cyclo*hexane, and one gram-molecule of hydrogen, the total pressure of the system can be calculated. In this calculation, it is assumed that there is no consumption or production of hydrogen after equilibrium has been established.

TABLE I

$G_T°$ *in kcal/mol*

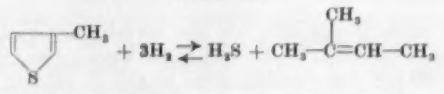
Compound	500° K	600° K	700° K	800° K	Lit.
3-Methylthiophene .	30·60	36·28	42·09	47·91	41
Hydrogen sulphide .	−15·44	−14·36	−13·25	−12·11	42
2-Methylbutane .	29·29	32·66	45·19	57·84	43
2-Methyl-2-butene .	31·82	41·03	50·42	59·94	44
Methylcyclohexane .	37·51	53·55	69·80	86·16	45
Toluene . . .	41·81	48·48	55·31	62·24	46

TABLE II

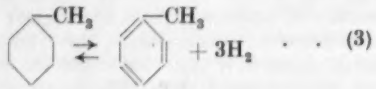


T, °K	$\Delta G_T°$, kcal/mol (of the reaction)	log K_p
500	−25·75	11·26
600	−17·98	6·55
700	−10·15	3·17
800	− 2·18	0·60

TABLE III

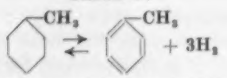


T, °K	$\Delta G_T°$, kcal/mol (of the reaction)	log K_p
500	−14·22	6·22
600	− 9·61	3·50
700	− 4·92	1·54
800	− 0·08	0·02



(3)

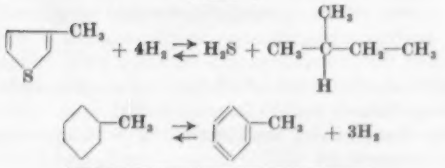
TABLE IV



T, °K	$\Delta G°_T$, kcal/mol (of the reaction)	log K_p
500	4·30	−1·88
600	− 5·07	+1·85
700	−14·49	+4·52
800	−23·92	+6·53

In Table V the total pressures have been calculated for the combination of equilibria (1) and (3), in Table VI for equilibria (2) and (3), for both equilibria groups on the condition that the quantity of hydrogen is constant (consumption = production).

TABLE V



T °K	log P_{total} (P in atm)
500	−3·06
600	−1·49
700	−0·37
800	+0·49

In all cases about 75 mol per cent of the sulphur compound has been transformed.

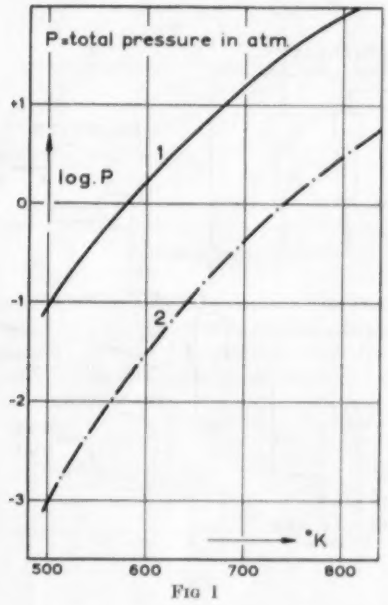
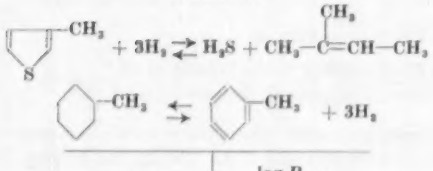


FIG 1

TABLE VI



T °K	log P_{total} (P in atm)
500	−1·02
600	+0·27
700	+1·20
800	+1·90

In this case the sulphur compound is almost completely transformed.

In Fig 1 the calculated values for the log P_{total} are graphically represented (*cf* Tables V and VI). In the calculations the deviations from the ideal gas laws are not taken into consideration.

In the "Autofining" process mineral oils are desulphurized by hydrogenation, whilst the necessary hydrogen is obtained by dehydrogenation of the naphthenes present in the feed. From the above it is clear that the dehydrogenation of the naphthenes will increase as the temperature becomes higher. Increase of pressure will retard the production of hydrogen. At a certain temperature a total pressure of the system can be calculated at which no production or consumption of hydrogen occurs. In fact, the equilibrium will not be completely established; side reactions also play a certain part.

EXPERIMENTAL

In the investigations of Hoog [34] Middle East gas oils were desulphurized; the influence of the contact time on the desulphurization was the chief subject of study. The experiments made by the authors in their laboratory show the influence of pressure, space velocity, and hydrogen–oil ratio on the desulphurization of gas oils, working under the conditions of a constant contact time and constant temperature. Some experiments refer to the aromatic hydrogenation which, especially at higher pressures, occurs during the desulphurization. Three Middle East gas oil fractions were used as feed in these investigations (Table VII).

TABLE VII

Middle East gas oil fractions	A	B	C
Boiling range, °C (1 atm)	250–350	250–350	295–305
Per cent by weight of sulphur	1·40	1·40	1·24
Average molecular weight	235	241	235
n_D^{20}	1·4722	1·4722	1·4678
d_4^{20}	0·8452	0·8453	0·8371

The hydrogen purity was 99·8 per cent vol. In all the experiments a Co–Mo–Al_2O_3 catalyst * was used.

The equipment used in this work is shown in Fig 2. Oil and hydrogen are introduced into the preheater; the oil evaporates. The hot vapours enter the reactor at the top. After cooling, the reaction mixture is then separated at the working pressure. The gas, chiefly hydrogen, is recirculated via the recycle gas pumps. The hydrogen consumption is balanced by supplementary fresh hydrogen. The liquid of the high pressure separator goes to a second low pressure separator. Here a part of the hydrogen sulphide and of the light hydrocarbons dissolved in the liquid is removed. At the beginning of the process hydrogen at the working pressure of the system is circulated. If the reactor and the preheater are at the desired temperature the oil feed is started.

* The authors render their thanks to the management of the Royal Dutch/Shell Laboratories in Amsterdam, from whom they obtained this catalyst.

Every experiment was carried out in duplicate. The volume of the catalyst in the reactor was always 300 ml. The rest of the content of the reactor was filled with 200 ml of glass beads. Two series of experiments were made: for the first series *cf* Tables VIII and IX, for the second series Tables XI and XII. Generally, the oil reacted in the gas phase. Only in one experiment (12 B and C) (Tables VIII and IX) could the oil partly pass the catalyst in the liquid phase. In all the experiments the cracking was unimportant, which, for example, was proved by the quantities of light hydrocarbons formed during the process, which

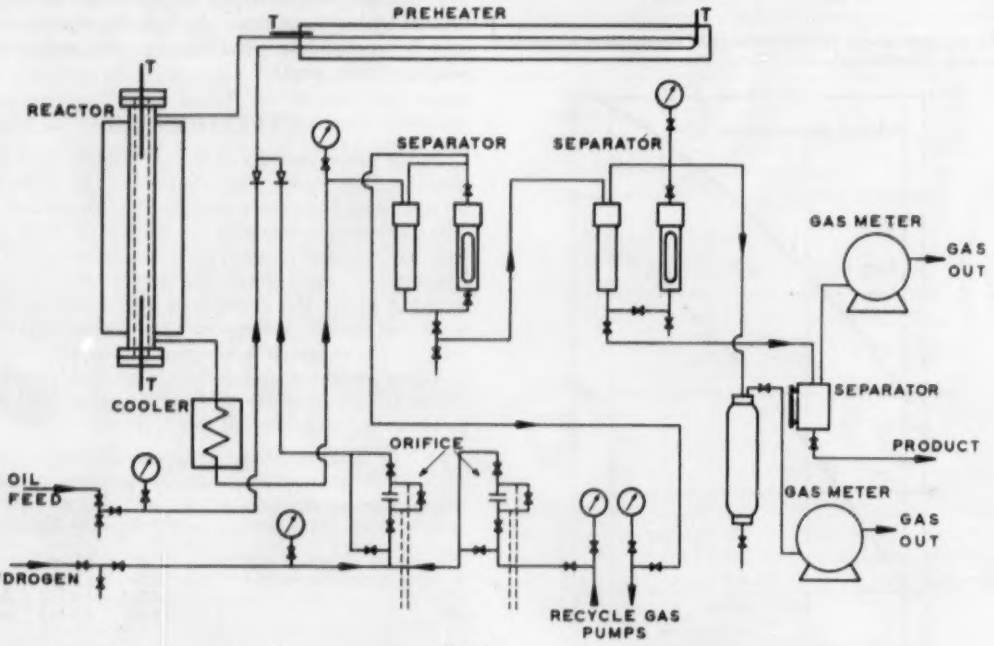


FIG 2

were only small. The material balances were satisfactory. Generally, the losses were smaller than 2 per cent, the total amount of products obtained being more than 98 per cent.

In the first series of experiments (Tables VIII and IX) gas oil feeds A and B were used. All the experiments of these series were made at about 375° C, the contact time being 9 seconds. This contact time was approximately calculated by means of the following formula:

$$t = \frac{PC_1}{(\text{W.H.S.V.})\,(\text{G.R.} + C_2)} \quad . \quad . \quad (4)$$

t = approximate contact time in seconds.
P = total pressure in atmospheres (atm abs).
W.H.S.V. = kilograms of oil/litre of catalyst/hr.
G.R. = hydrogen introduced in litres (1 atm abs and 1° C)/kg of oil feed.
C_1 and C_2 = constants, dependent on the temperature, the average molecular weight of the gas oil, etc.

Formula (4) is not absolutely exact; the influence of some factors had to be estimated.

For comparison, the formula is quite appropriate. At a temperature of 375° C constants C_1 and C_2 for the gas oils in question are given in Table X.

The partial pressures were calculated taking the ideal gas laws as a basis. The effective partial pressures will be different.

To obtain an opinion of the desulphurization, the percentage of sulphur retention was calculated.

$$\%\ \text{sulphur retention} = \frac{\%\ \text{of wt of sulphur in the produced oil}\ ^*}{\%\ \text{of wt of sulphur in the gas oil feed}}\ 100\% \quad . \quad (5)$$

If there is no desulphurization at all, the percentage of sulphur retention is 100. Before the sulphur determination was carried out in the resultant liquid product the dissolved hydrogen sulphide was washed out with caustic soda.

In Figs 3 to 8 the result of the experiments of the first series (Tables VIII and IX) are graphically represented. Increase of hydrogen pressure favours the desulphurization, although the effect above 50 atm abs is not great (Figs 3 and 4). At constant hydrogen pressure the sulphur removal is better at low W.H.S.V.

* Free from H_2S.

than at high space velocity (Figs 4, 5, 6, and 8). This can easily be understood, because in the case of high L.H.S.V. the quantity of hydrogen in proportion to the quantity of oil is smaller (contact time being constant). In Hoog's investigations [34] it has been found that the gas oils can only be desulphurized to a certain percentage weight of S in the reaction product. With long contact time, too, not more than 95 per cent of the sulphur compounds were transformed. In the authors' experiments it seems that certain sulphur compounds in the gas oil do not react with the Co–Mo–Al_2O_3 catalyst under the conditions of the experiments. The

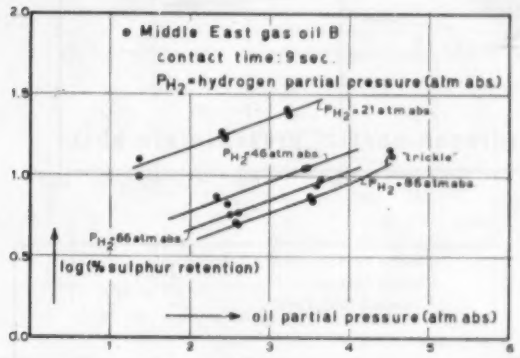


FIG 3

explanation of this phenomenon is, for instance, the adsorption to a great extent of special types of sulphur compounds, so that the reaction with hydrogen is practically excluded. The total aspect of the desul-

TABLE VIII

No. of experiment	Gas oil	Duration of experiment, hr	Reactor temp, °C	Pressure, atm abs	Standard litres of gas/kg of feed	W.H.S.V., kg of feed/litre of catalyst/hr	Contact time, sec	Log (% sulphur retention)
1	A	13– 21	369	51·0	3500	1·50	9·5	0·52
2	A	21– 26	378	50·0	2700	1·92	9·3	0·56
3B	B	36– 42	378	26·0	900	3·03	8·6	1·24
3C	B	42– 48	379	26·0	900	2·98	8·8	1·27
4B	B	54– 60	374	51·0	1950	2·73	9·2	0·87
4C	B	60– 66	377	51·0	1850	2·89	9·1	0·82
5B	B	72– 78	376	71·0	2550	2·90	9·3	0·76
5C	B	78– 84	376	71·5	2450	3·01	9·3	0·77
6B	B	90– 96	374	91·0	3200	2·94	9·4	0·71
6C	B	96–102	374	91·0	3200	2·98	9·3	0·70
7B	B	108–112	374	91·0	2300	4·13	9·2	0·84
7C	B	113–116	375	90·5	2350	4·07	9·1	0·87
8B	B	122–126	374	71·0	1750	4·26	9·1	0·94
8C	B	126–130	374	71·0	1750	4·31	8·9	0·97
9B	B	136–140	375	51·0	1300	4·19	8·7	1·05
9C	B	140–144	377	51·0	1300	4·15	8·8	1·04
10B	B	150–154	375	26·0	650	4·25	8·2	1·38
10C	B	154–158	374	26·0	650	4·19	8·4	1·41
11B	B	165–169	375	26·0	1700	1·59	9·1	1·00
11C	B	169–173	374	26·0	1700	1·59	9·1	1·11
12B	B	178–182	375	91·0	1800	5·37	8·9	1·16
12C	B	182–186	374	91·0	1800	5·39	8·9	1·12
13B	A	194–198	377	51·0	2550	2·08	9·3	0·78

phurization in this first series of experiments is comparable with the results of Hoog's experiments.[34]

In the authors' second series of experiments (Tables XI and XII) gas oils B and C were used. The temperature was also 375° C, the approximate contact time being 9 seconds. An interesting feature is the low sulphur content of all the liquid products formed. It

TABLE IX

No. of experiment	Partial vapour pressures, atm abs				Standard litres of hydrogen/kg of feed	$\frac{1}{\text{W.H.S.V.}}$	$\frac{1}{P_{H_2}}$
	Gas oil	H_2	H_2S	Light hydrocarbons			
1	1·35	45·05	1·1	3·5	3200	0·667	0·0222
2	1·70	43·6	1·1	3·6	2450	0·521	0·0230
3B	2·44	20·9	1·2	1·5	800	0·320	0·0478
3C	2·44	20·9	1·2	1·5	800	0·335	0·0478
4B	2·32	46·8	1·2	0·7	1850	0·368	0·0214
4C	2·44	46·7	1·2	0·7	1800	0·346	0·0214
5B	2·30	66·1	1·2	1·2	3450	0·345	0·0151
5C	2·61	66·7	1·1	1·1	3250	0·332	0·0150
6B	2·57	85·8	1·6	1·0	3100	0·340	0·0117
6C	2·57	85·8	1·6	1·0	3100	0·335	0·0117
7B	3·51	85·6	0·9	0·8	2350	0·342	0·0117
7C	3·44	85·4	0·9	0·8	2300	0·346	0·0117
8B	3·58	65·5	0·95	0·95	1700	0·255	0·0153
8C	3·58	65·5	0·95	0·95	1700	0·232	0·0153
9B	3·41	46·0	0·7	0·9	1280	0·239	0·0218
9C	3·41	46·0	0·7	0·9	1280	0·241	0·0218
10B	5·25	21·15	1·1	0·5	600	0·255	0·0473
10C	5·25	21·15	1·1	0·5	600	0·259	0·0473
11B	1·55	21·5	1·2	1·95	1800	0·629	0·0465
11C	1·55	21·5	1·2	1·95	1800	0·629	0·0465
12B	4·46	85·3	0·7	0·5	1750	0·186	0·0118
12C	4·46	85·3	0·7	0·5	1750	0·186	0·0117
13B	1·83	44·25	1·2	3·7	2300	0·481	0·0226

TABLE X

Middle East gas oil fraction .	A	B	C
C_1	1000	1000	1000
C_2	95	93	95

is probable that the initial activity of the catalyst in this series of experiments is not lost as quickly as in the first series. In the first series, the experiments were started with gas oil A. In contrast to oils B and C, A was not a freshly distilled oil. If a comparison of the sum of the partial pressures of the light hydrocarbons is made, using the different gas oils as raw materials, it is clear that these partial pressures are distinctly high for gas oil A, which indicates considerable cracking.

The more intense cracking of gas oil A may be a result of the activity of unstable oxidation products. These oxidation products might have been formed in the oil by the action of oxygen from the air. Generally, cracking is connected with the deposition of coke on the catalyst, which is the reason for the decline in catalyst activity. In the second series of experiments only freshly distilled oils were used. Compared with the first series a better desulphurization was obtained.

For comparison a 24-hr experiment was carried out with gas oil B as raw material and under the same conditions as experiment 14B (second series) but without any catalyst. The reactor was filled with 500 ml of glass beads. The sulphur retention in this case was higher than 90 per cent (*cf* Table XIII).

Especially at higher pressures the hydrodesulphurization will be combined with aromatic hydrogenation. To study this more thoroughly the liquid reactions products were fractionated. The fractions boiling above 200° C were investigated by the n–d–M and the n–d–V_K method.[47, 48] By adsorption of the gasoline fractions on silica gel the percentages by volume of aro-

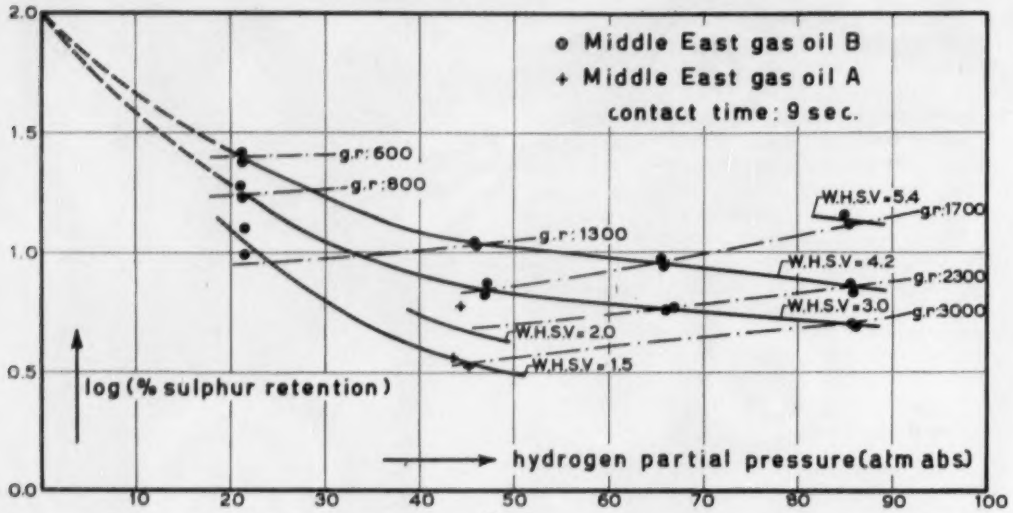


FIG 4

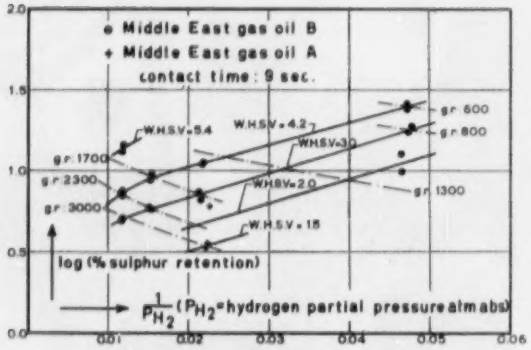


FIG 5

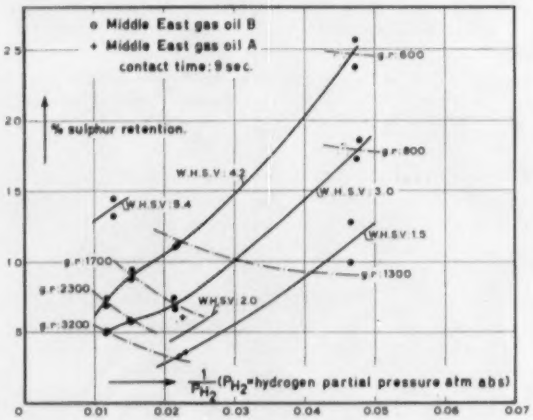


FIG 6

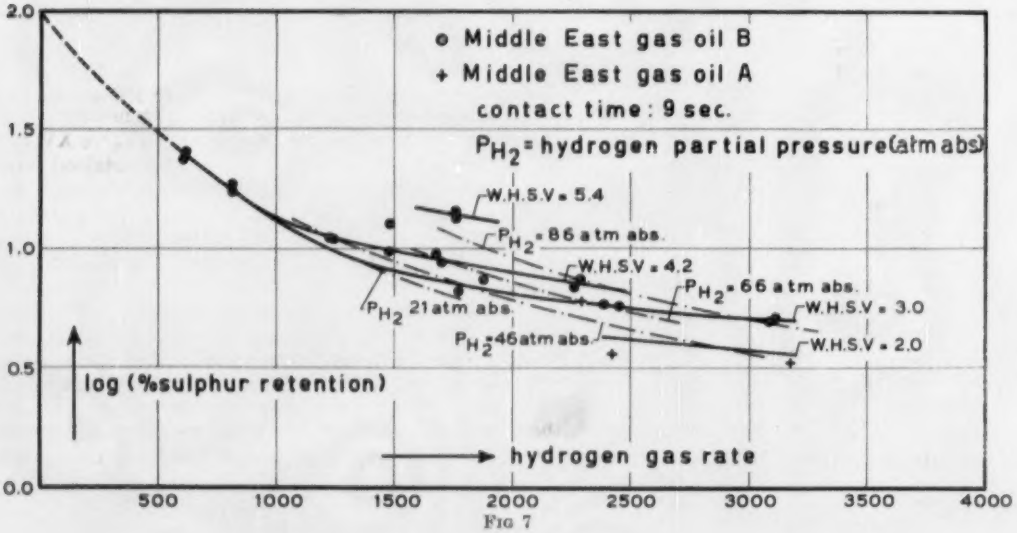

o Middle East gas oil B
+ Middle East gas oil A
contact time: 9 sec.
P_{H_2} = hydrogen partial pressure (atm abs)
W.H.S.V = 5.4
P_{H_2} = 86 atm abs.
W.H.S.V = 4.2
P_{H_2} = 66 atm abs.
W.H.S.V = 3.0
P_{H_2} 21 atm abs.
P_{H_2} = 46 atm abs.
W.H.S.V = 2.0
log (% sulphur retention)
hydrogen gas rate

FIG 7

matics, alkenes, and alkanes + naphthenes respectively were determined.[49] By comparing the distillation curves of the feed and the products obtained therefrom it was proved that 9 to 13 per cent weight of the products boiled below the initial boiling point (about 250° C) of the corresponding feed. These low boiling products, chiefly gasoline, contained 20 to 30 per cent volume of aromatic. At lower pressures more light hydrocarbons were formed than at high pressure. If it is assumed that the sulphur compounds in the oil contain one sulphur atom per molecule, the percentage by weight of sulphur compounds can be calculated by

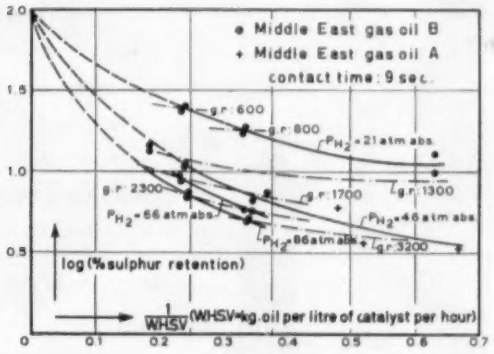


FIG 8

means of the percentage of S and the average molecular weight of the oil. Thus for gas oils B and C 10·5 and 9 per cent by weight of sulphur compounds are found respectively. The light hydrocarbons are formed from the sulphur compounds (8 to 9 per cent by weight of the oil), and by cracking (at most 5 per cent by weight of the oil). At high pressure hydrogenation of aromatics takes place to a small extent.

TABLE XI

No. of experiment	Gas oil	Duration of experiment, hr	Reactor temp, °C	Pressure, atm abs	Standard litres of gas/kg of feed	W.H.S.V., kg of feed/litre of catalyst/hr	Contact time, sec	Log (% sulphur retention)
14B	B	18–24	375	51·0	1480	3·62	9·1	0·73
15B	B	30–36	375	91·0	2750	3·55	9·0	0·27
15C	B	36–42	375	91·0	2800	3·51	9·0	0·20
16B	B	50–57	373	51·0	4550	1·25	8·9	0·11
16C	B	57–64	375	51·0	4650	1·21	9·1	0·13
17B	B	70–76	375	91·0	4600	2·15	9·0	0·22
17C	B	76–82	376	91·0	4600	2·15	9·0	0·32
18B	B	88–94	375	151·0	4600	3·59	9·0	0·41
18C	B	94–97·5	377	151·0	4650	3·52	9·0	0·40
19B	C	103·5–106·5	377	151·0	5500	3·00	9·0	−0·22
19C	C	110–116	374	151·0	5450	3·01	9·0	−0·16
20B	C	120·5–124·5	375	91·0	3250	2·97	9·2	−0·22
20C	C	124·5–128·5	375	91·0	3300	2·99	9·0	−0·07
21B	C	136–140	376	45·5	1550	3·06	9·0	0·19
21C	C	140–143	375	45·5	1600	3·00	8·9	0·27
22B	C	150–155	373	45·5	3300	1·49	9·0	0·11
22C	C	155–160	376	45·5	3250	1·49	9·1	0·14
23B	B	167–173	375	51·0	1450	3·63	9·1	0·80

Table XIV gives some physical constants of the products which are obtained by desulphurization from feed C. The gasoline has been removed by distillation. By means of the n–d–M and the n–d–V_K method the average number of rings per molecule R_T and the

TABLE XII

No. of experiment	Partial pressures in reaction gas, atm abs				Standard litres of hydrogen/kg of feed	$\frac{1}{\text{W.H.S.V.}}$	$\frac{1}{p_{H_2}}$
	Gas oil	H_2	H_2S	Light hydrocarbons			
14B	3·05	46·9	0·1	1·0	1400	0·276	0·0213
15B	2·97	85·9	0·1	2·1	2700	0·282	0·0116
15C	2·94	85·9	0·1	2·1	2700	0·285	0·0116
16B	1·02	47·8	0·1	2·1	4350	0·813	0·0209
16C	1·01	47·8	0·1	2·1	4450	0·826	0·0209
17B	1·80	87·0	0·1	2·1	4500	0·465	0·0115
17C	1·80	87·0	0·1	2·1	4500	0·465	0·0115
18B	2·98	145·8	0·1	2·1	4350	0·279	0·00686
18C	2·95	145·9	0·1	2·1	4600	0·284	0·00685
19B	2·57	146·8	0·4	1·3	5450	0·333	0·00681
19C	2·59	146·8	0·4	1·3	5400	0·332	0·00681
20B	2·58	85·6	1·4	1·4	3150	0·337	0·0117
20C	2·55	85·7	1·4	1·4	3200	0·334	0·0117
21B	2·61	40·3	1·1	1·4	1450	0·327	0·0248
21C	2·58	40·4	1·1	1·4	1500	0·333	0·0247
22B	1·29	41·4	1·0	1·5	3100	0·671	0·0242
22C	1·30	41·4	1·0	1·8	3050	0·671	0·0242
23B	3·05	45·6	1·4	1·0	1400	0·275	0·0219

TABLE XIII

No. of experiment	Feed	Reactor		Standard litres of gas/kg of feed	Feed, kg/hr	Log (% sulphur retention)	Partial pressure atm abs			
		Temp, °C	Pressure, atm abs				Oil	H_2	H_2S	Light hydrocarbons
24B	B	375	51·0	1400	1·115	1·96	3·21	47·7	0·0	0·1
24C	B	375	51·0	1400	1·099	1·98	3·15	47·8	0·0	0·1

TABLE XIV

No. of experiment	M	V_K^{20}, centistokes	n_D^{20}	d_4^{20}	% S
19B	238	5·67	1·4573	0·8201	nil
19C	238	5·67	1·4573	0·8204	,,
20B	237	5·44	1·4590	0·8215	,,
20C	243	5·42	1·4591	0·8217	,,
21B	235	5·46	1·4623	0·8249	,,
21C	238	5·34	1·4622	0·8246	,,
22B	231	5·03	1·4631	0·8245	,,
22C	236	5·12	1·4642	0·8253	,,
Oil C . .	235	—	1·4678	0·8371	1·24
Oil C (gasoline free) .	241	6·13	1·4680	0·8380	1·26

average number of aromatic rings per molecule R_A can be calculated from the physical constants given in Table XIV. The results are given in Table XV. For comparison, gas oil C and a fraction obtained from C by an analogous distillation, as done with the products of the process, are also analysed. The results are found in Table XV. The aromatic content decreases at higher pressures, although the differences are small.

The percentages by volume of the aromatics, alkenes, and alkanes + naphthenes of the light hydrocarbons of these experiments are shown in Table XVI.

At high pressure the gasoline fractions formed during the process contain more aromatics than at lower pressure. In the first case, less gasoline is formed. The light hydrocarbons formed by cracking will not be as rich in aromatics as the hydrocarbons

TABLE XV

No. of experiment	n–d–M		n–d–V_K		Pressure, atm abs (Table XI)
	R_T	R_A	R_T	R_A	
19B	0·85	0·20	0·90	0·20	151·0
19C	0·85	0·20	0·90	0·20	151·0
20B	0·85	0·25	0·90	0·25	91·0
20C	0·80	0·25	0·90	0·25	91·0
21B	0·80	0·35	0·90	0·35	45·5
21C	0·80	0·35	0·90	0·35	45·5
22B	0·80	0·40	0·90	0·40	45·5
22C	0·75	0·40	0·85	0·40	45·5
Oil C	0·80	0·35	—	—	—
Oil C (gasoline free)	0·85	0·35	0·90	0·35	—

TABLE XVI

No. of experiment	% by volume of aromatic	% by volume of alkene	% by volume of alkane + naphthene	Pressure, atm abs (Table XI)
19B	34	2	64	151·0
19C	34	2	64	151·0
20B	24	2	74	91·0
20C	24	2	74	91·0
21B	21	1	78	45·5
21C	21	1	78	45·5
22B	28	1	71	45·5
22C	24	1	75	45·5

which are formed from the sulphur compounds. At lower pressure, the cracking of the gas oil will be stronger, the result being a decrease of the aromatic content in the gasoline fractions.

CONCLUSIONS

Middle East gas oils were desulphurized by catalytic hydrogenation over a Co–Mo–Al_2O_3 catalyst. At a constant contact time and constant temperature, it was proved that the weight hourly space velocity and the total pressure influence the degree of desulphurization. Increase of pressure decreases the sulphur retention of the oil; an increase of the weight hourly space velocity lowers desulphurization. The catalyst was selective. At higher pressures (up to 150 atm) hydrogenation of aromatics took place to a small extent. The gasoline fractions formed during hydrodesulphurization are rich in aromatics (20 to 35 per cent, by volume). The cracking was unimportant and took place even at the lower pressures to the extent of only a few per cent.

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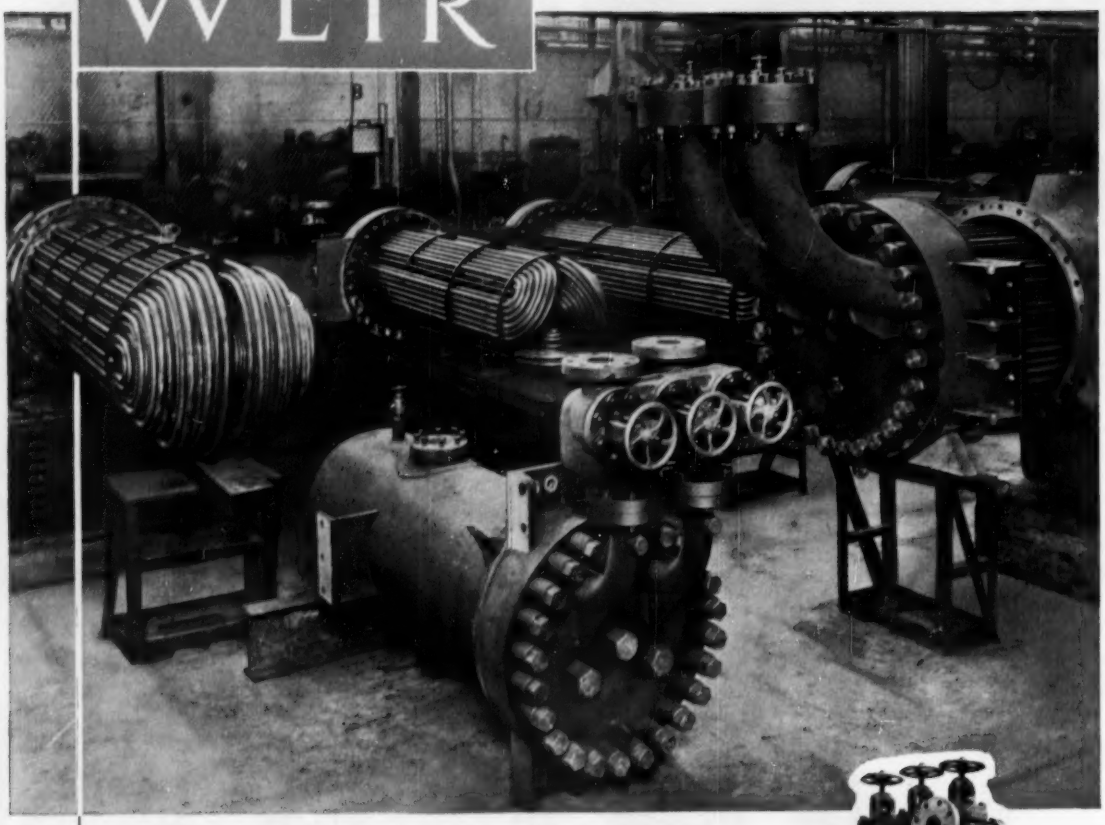

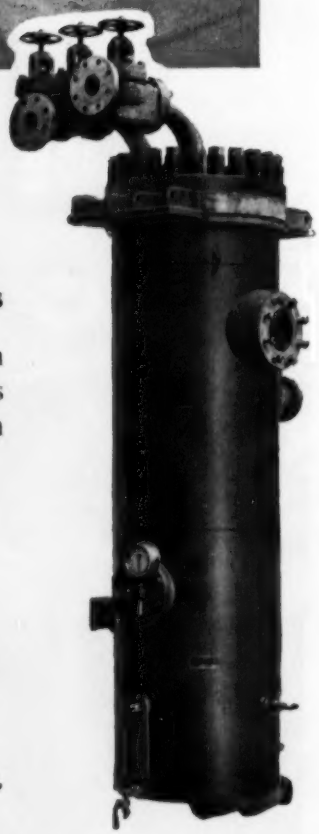

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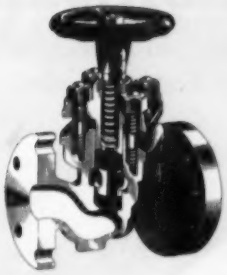

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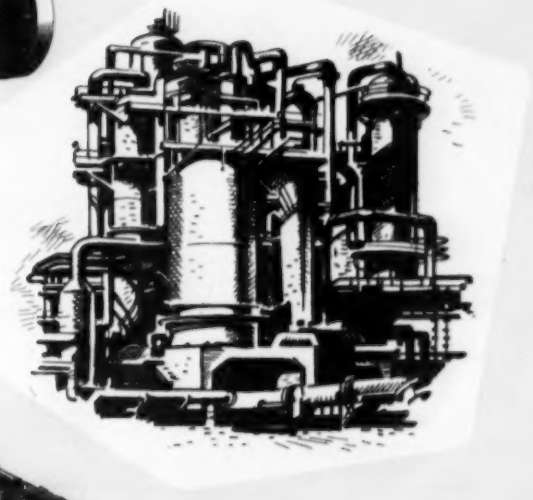

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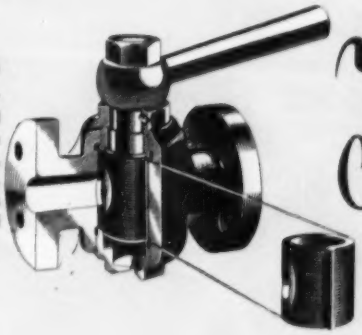

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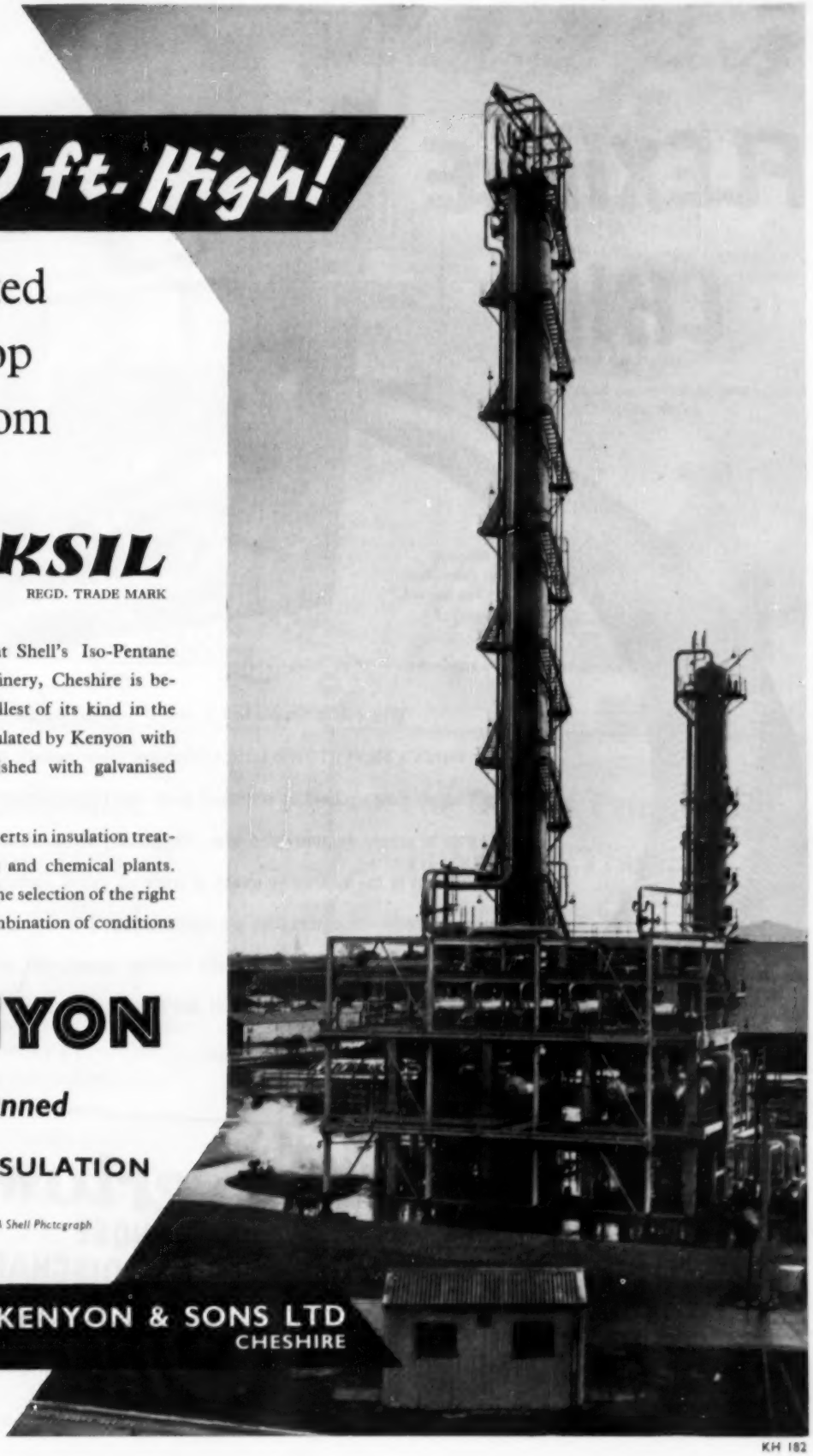

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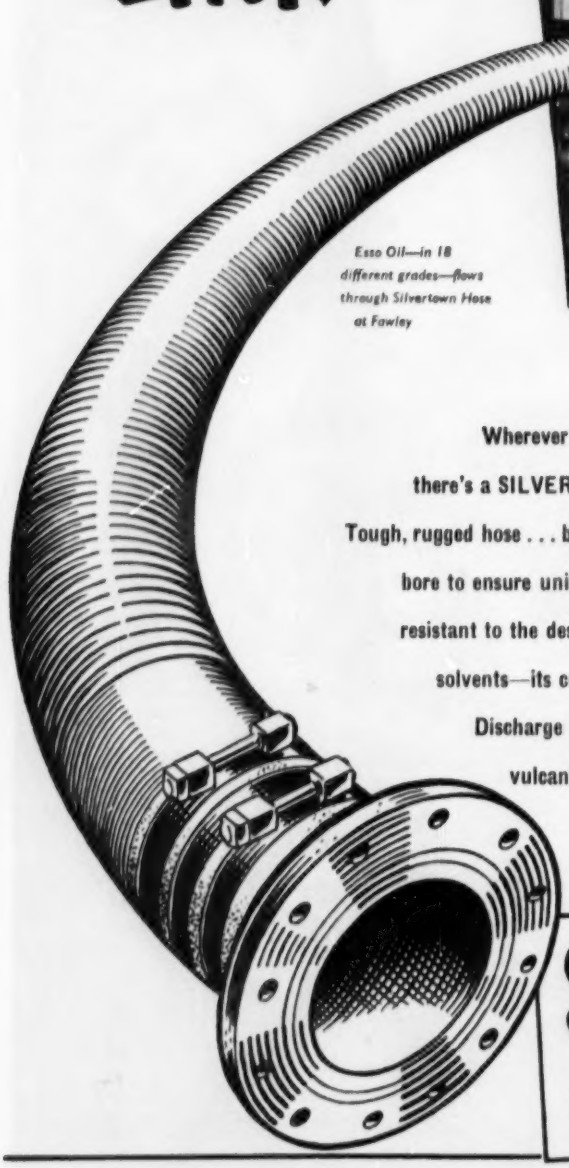

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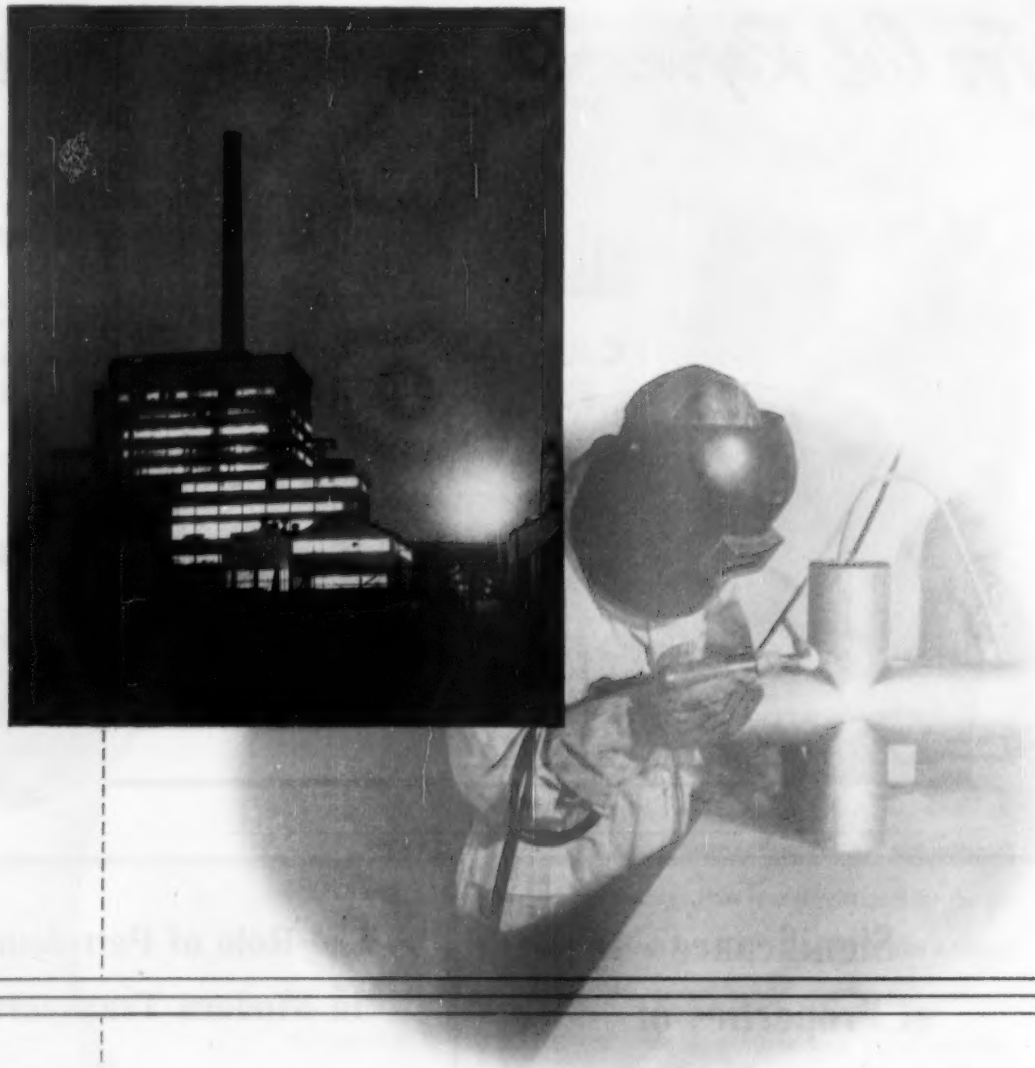

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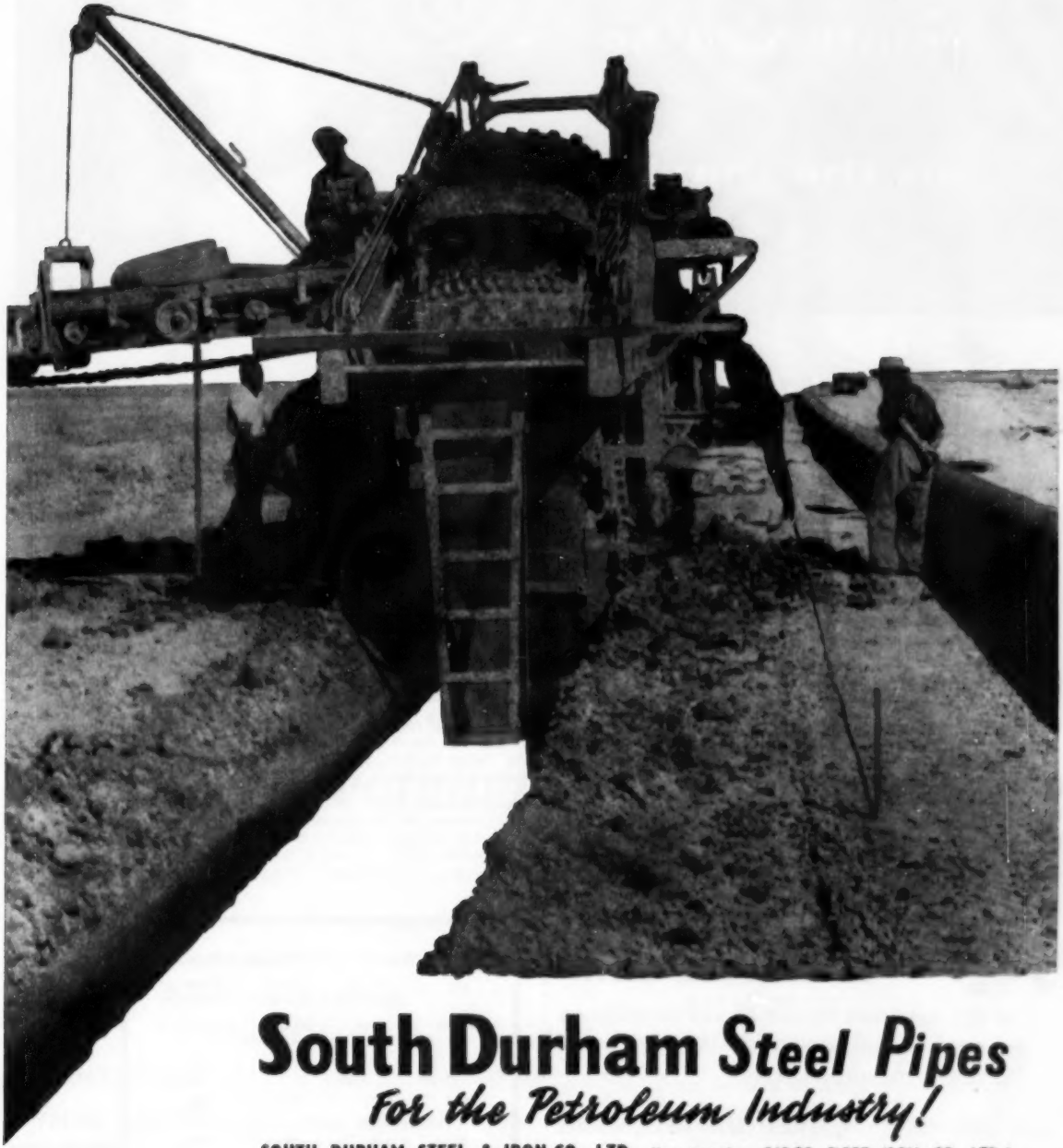

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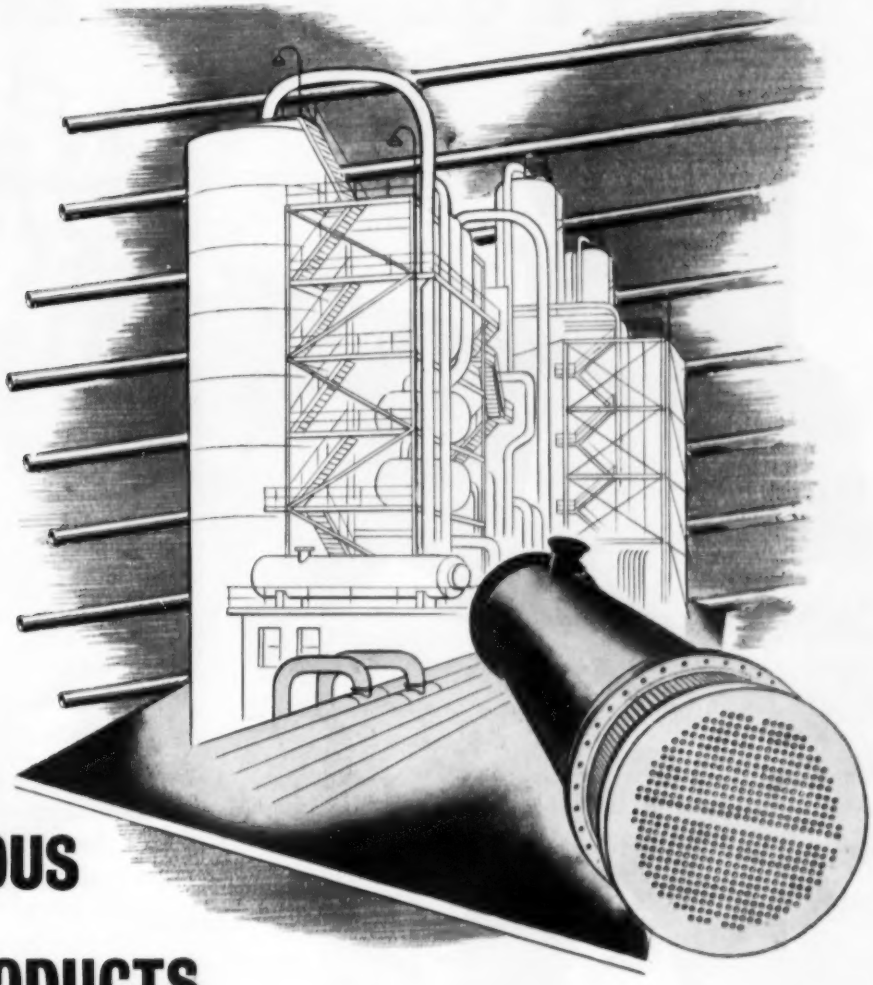

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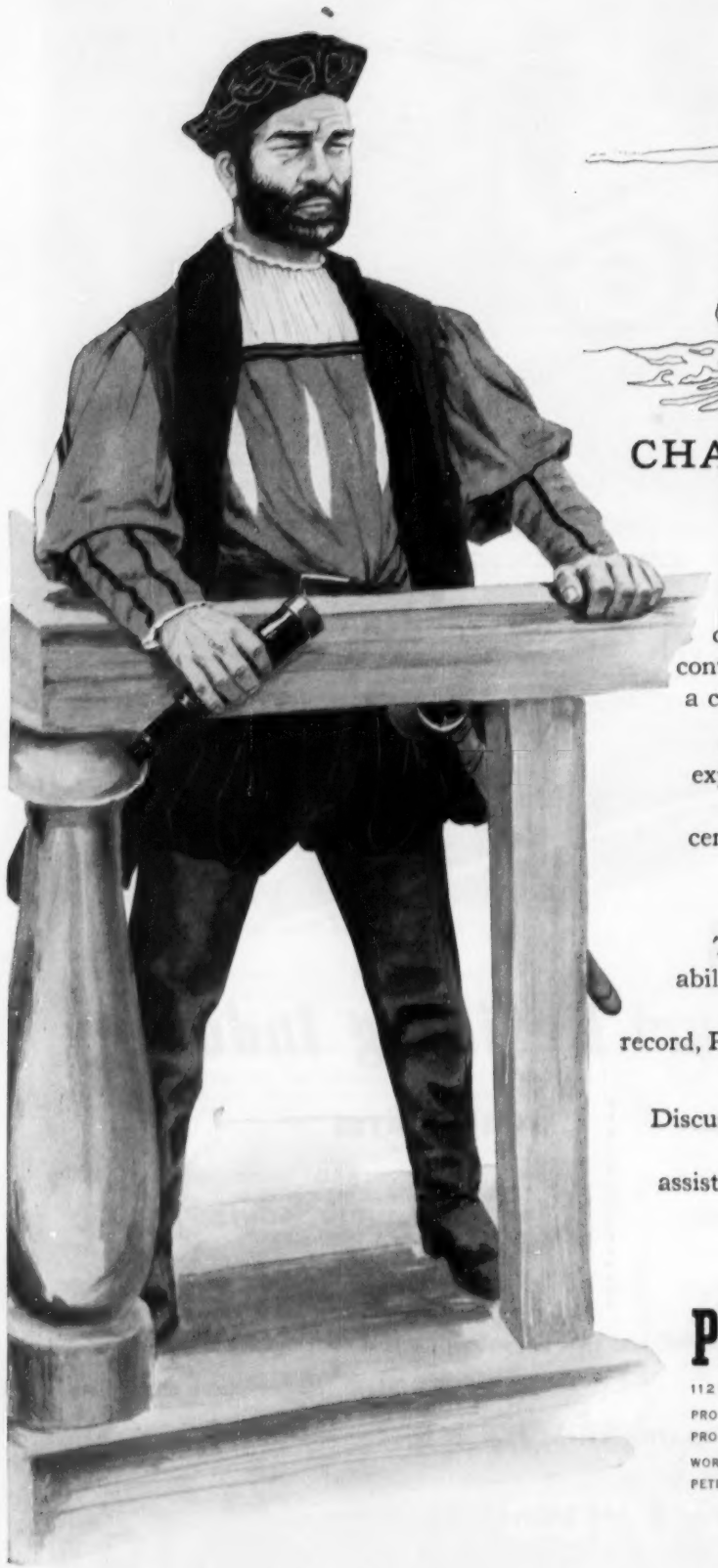

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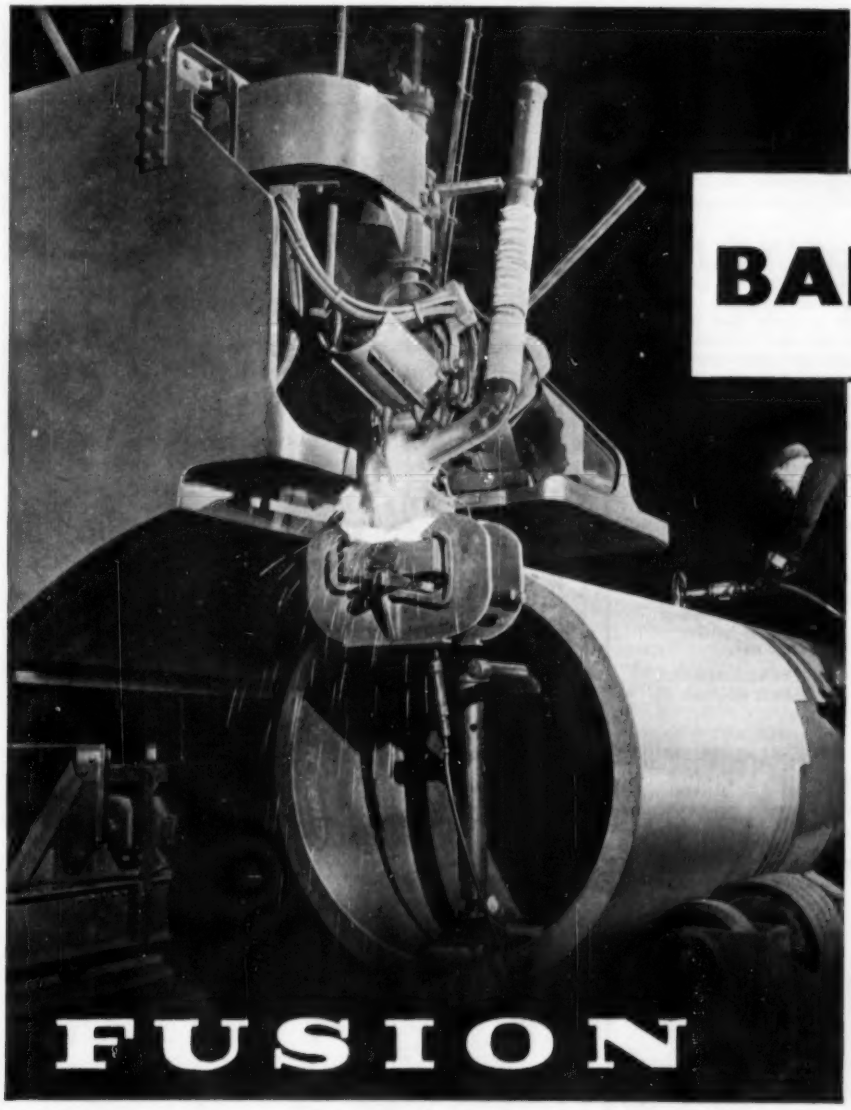

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Information received and not checked led us to write on pages 160 and 180 of our book *Les Derives du Petrole* (Blondel and Rougery, Paris, 1952) the following remarks on Elektrion or Voltol oils manufactured by the Hemptinne process:

> ". . . because of the presence of fatty oils, the saponification value and the increasing acidity (of these oils) present certain disadvantages. In any case, they cannot be used for modern bearings."
> "These oils whose manufacture is costly, have all the defects of fatty oils. They have had very little success, and with the appearance of bright stocks they have disappeared from the market. . . ."

We now acknowledge that we have made an error both in our criticism of these oils and in declaring that they have disappeared from the markets.

> The technical data we have read in a notice published by the Société De Cavel & Roegiers entitled *Notice Elektrion R Concentrée* and:
> The results of tests carried out on the bench on various engines by the Institut Français du Pétrole, and finally:
> The fact that import quotas for France and French possessions overseas covering concentrated Elektrion oil (designed by name in the Franco-Belgian trade agreements) amount to over one hundred million francs per annum,

oblige us to acknowledge our error and to withdraw the above texts. We do so most willingly and ask the Société De Cavel & Roegiers to accept our apologies.

Signed: E. FOURET
M. BLANCHIER

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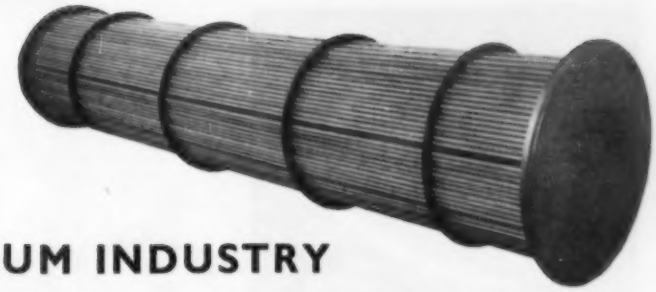

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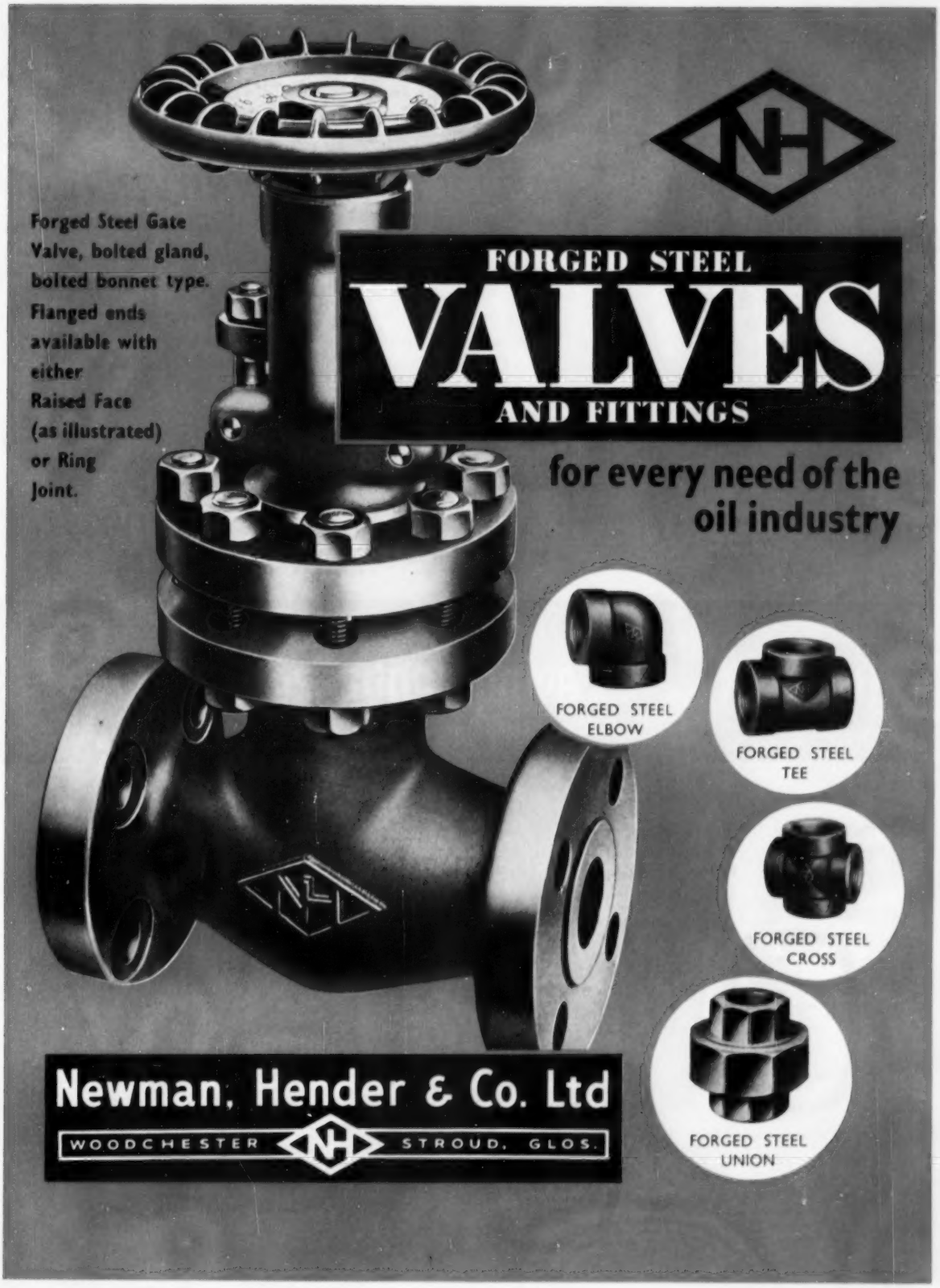
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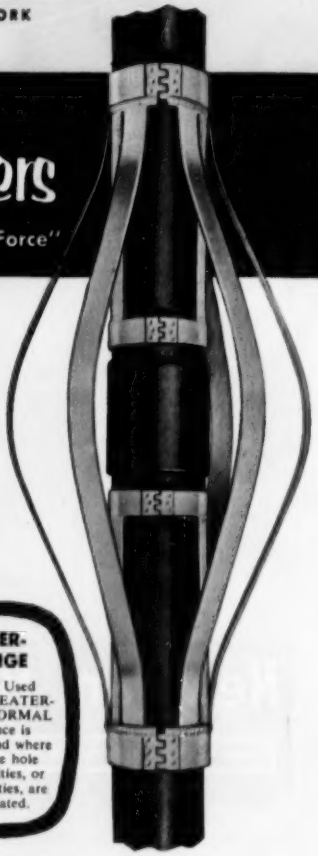

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